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(71) Applicant (for all designated States except US): FUJI PHOTO FILM CO., LTD. [JP/JP]; 210, Nakanuma, Minami-Ashigara-shi, Kanagawa 250-0123 (JP).

(72) Inventors; and

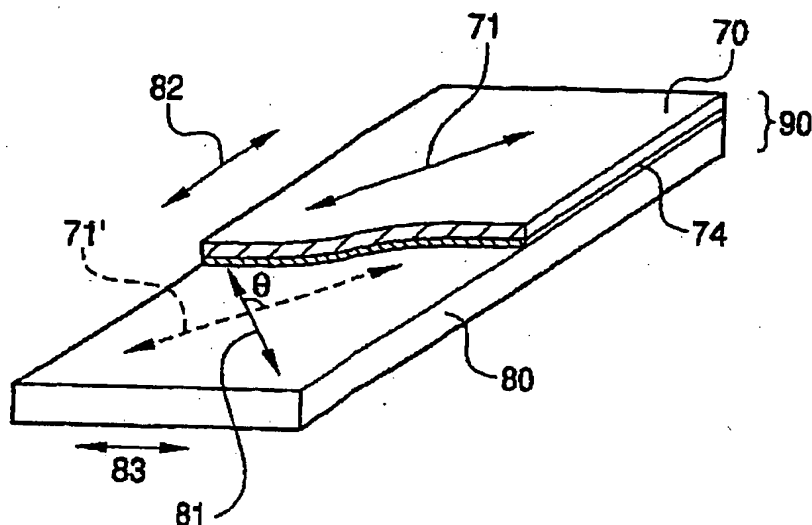
(75) Inventors/Applicants (for US only): TAGUCHI, Keiichi [JP/JP]; c/o Fuji Photo Film Co., Ltd., 210, Nakanuma, Minami-ashigara-shi, Kanagawa 250-0123 (JP). KITAKOUJI, Hiromoto [JP/JP]; c/o Fuji Photo Film Co., Ltd., 210, Nakanuma, Minami-ashigara-shi, Kanagawa 250-0123 (JP). SHIRATSUCHI, Kentaro [JP/JP]; c/o Fuji Photo Film Co., Ltd., 210, Nakanuma, Minami-ashigara-shi, Kanagawa 250-0123 (JP).

(74) Agents: OGURI, Shohei et al.; Elkoh Patent Office, 28th Floor, Ark Mori Building, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6028 (JP).

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(54) Title: POLARIZING PLATE, PRODUCTION METHOD THEREOF AND LIQUID CRYSTAL DISPLAY USING THE SAME



(57) Abstract: The present invention can provide a polarizing plate excellent in the dimensional stability, particularly in the aging stability, a method for easily producing a polarizing plate, being capable of improving the yield in the step of punching the polarizing plate, and a liquid crystal display having excellent display grade at a low cost, and a polarizing plate of the present invention, comprising: a polarizing film; and a protective film attached to at least one surface of the polarizing film, wherein the angle made by the stretching axis of the protective film and the stretching axis of the polarizing film is no less than 10° and less than 90°



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## DESCRIPTION

POLARIZING PLATE, PRODUCTION METHOD THEREOF AND LIQUID  
CRYSTAL DISPLAY USING THE SAME

## Technical Field

5           The present invention relates to a polarizing plate having excellent dimensional stability, a production method thereof and a liquid crystal display using the polarizing plate.

## Background Art

10           With the popularization of a liquid crystal display (hereinafter referred to as "LCD"), demands for a polarizing plate are abruptly increasing. The polarizing plate generally comprises a polarizing film having a polarizing ability and a protective film attached to both  
15 surfaces or one surface of the polarizing film through an adhesive layer.

          The material used for the polarizing film is mainly polyvinyl alcohol (hereinafter referred to as "PVA"). A PVA film is monoaxially stretched and then dyed with iodine  
20 or a dichromatic dye or dyed and then stretched and this film is further crosslinked with a boron compound to form a polarizing film. The polarizing film is usually produced by stretching (longitudinally stretching) a continuous film along the running direction (longitudinal direction) and

therefore, the absorption axis of the polarizing film is almost in parallel to the longitudinal direction.

On the other hand, the protective film attached at least to one surface of the polarizing film is demanded to have low retardation because if it has a birefringence, the polarizing state changes. However, the retardation disadvantageously increases depending on the temperature and humidity in the environment and this problem has been heretofore solved by attaching the protective film such that the phase lag axis of the protective film runs perpendicularly to the transmission axis of the polarizing film (that is, the phase lag axis of the protective film runs in parallel to the absorption axis of the polarizing film).

However, in this case, since the phase lag axis of the protective film and the absorption axis of the polarizing film are in parallel to each other, the dimensional stability is poor, particularly, there is a problem in the aging stability.

On the other hand, in conventional LCD, the polarizing plate is disposed by inclining its transmission axis at  $45^\circ$  with respect to the vertical or transverse direction of a picture plane and therefore, if the polarizing film is produced by longitudinally or transversely stretching the film as described above, the

polarizing plate produced in a roll form must be punched at a 45° direction with respect to the longitudinal direction of the roll in the punching step. In this case, the yield decreases or the polarizing plate material after lamination is difficult to reuse, as a result, the waste disadvantageously increases. In order to solve this problem, a method of obtaining a polarizing film by inclining the orientation axis of a polymer at a desired angle with respect to the film transportation direction has been proposed (see, JP-A-2000-9912 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-3-182701).

By this method, a polarizing film having an absorption axis not in parallel to the longitudinal direction can be theoretically obtained, however, since the film travelling speed differs between the left and the right of film at the time of stretching a plastic film, the film is drawn or wrinkled and it is very difficult to produce a polarizing film having a desired tilt angle (45° in the polarizing plate). Thus, this method is not practiced.

For the protective film, cellulose triacetate is mainly used because this film is optically transparent and small in the birefringence. The polarizing film is usually produced by monoaxially stretching a continuous film in the

running direction (longitudinal direction) and therefore, the absorption axis of the polarizing film is almost in parallel to the longitudinal direction.

Furthermore, when another optical member, for example, a  $\lambda/4$  plate is attached, this must be attached every each panel and the process is cumbersome. In addition, a production step of laminating a plurality of films while strictly controlling the angle is necessary and due to sliding of angles, light leakage is generated to cause a phenomenon that the color display in the black part changes into yellow or blue. Thus, roll-to-roll attaching is demanded.

In recent years, the liquid crystal display is not only used in doors but its outdoor use is also increasing. Examples of the outdoor use include a large display for the purpose of street advertisement, a liquid crystal display for car navigation mounted on vehicles, and mobile medium liquid crystal display represented by cellular phone. Accompanying this change in the use environment, demand for a liquid crystal display not changing in the color and reduced in the fluctuation of transmittance and polarization degree even under high-temperature high-humidity conditions is pressing. By this change, the polarizing plate is also demanded to satisfy the requirement that the transmittance and color in the entire

picture plane of a display are less changed even in a high-temperature high-humidity environment.

In order to solve this problem, as described above, several methods have been proposed where the orientation  
5 axis of the polymer is inclined at a desired angle with respect to the film conveying direction (JP-A-2000-9912).

JP-A-3-182701 discloses a method of producing a film having a stretching axis at an arbitrary angle  $\theta$  with respect to the film running direction by using a mechanism  
10 where a plurality of laterally paired film-holding points each making an angle  $\theta$  to the running direction are provided at both side edges of a continuous film and each pair of points can stretch the film to the  $\theta$  direction as the film runs. Also in this method, since the film  
15 travelling speed differs between left and right of the film, drawing or wrinkling is generated on the film and for releasing this, the stretching step must be greatly prolonged, which gives rise to a problem that the equipment cost increases.

20 JP-A-2-113920 discloses a production method of stretching the film in the direction obliquely crossing the machine direction of film by running the film while gripping both edges thereof between chucks aligned in two rows and running on tenter rails disposed such that the  
25 chucks run different distances in a predetermined running

section. Also in this method, drawing or wrinkling is generated at the oblique stretching and this is disadvantageous for the optical film.

Furthermore, these stretching methods have a  
5 fundamental problem that the stretching axis inclines mainly due to bowing generated when the film leaves the tenter clips.

Korean Unexamined Patent Publication P2001-005184 discloses a polarizing plate where the absorption axis is  
10 inclined by a rubbing treatment. However, as generally known, the regulation of orientation by rubbing is effective only in the range from the film surface to at most a nano-order portion and a polarizer such as iodine or dichromatic dye cannot be satisfactorily oriented, as a  
15 result, the polarizing performance is disadvantageously poor.

As other conventional methods, JP-A-6-167611 discloses a liquid crystal display using a polarizing plate reduced in the shrinkage percentage under high-temperature  
20 high-humidity conditions. JP-A-12-035512 discloses a polarizing plate reduced in the change of transmittance at high temperatures by controlling the addition of zinc, the polymerization degree of PVA and the saponification degree of PVA. Also, JP-A-13-083329 discloses an iodine  
25 polarizing film reduced in the deterioration of polarizing



performance under high-temperature high-humidity conditions by specifying the pH value of a boric acid-containing aqueous solution. However, these are insufficient to satisfy the purpose of improving the durability.

5

#### Disclosure of the Invention

Accordingly, the object of the present invention is to provide a polarizing plate having excellent dimensional stability, particularly aging stability.

10 Another object of the present invention is to provide a long polarizing plate in a roll form, which is excellent in the dimensional stability and improved in the yield in the step of punching a polarizing plate.

Another object of the present invention is to provide  
15 an inexpensive long polarizing plate reduced in the dispersion of the stretching axis, which is composed of an obliquely stretched polarizing film capable of improving the yield in the step of punching the polarizing plate.

Another object of the present invention is to provide  
20 a high-performance and inexpensive polarizing plate reduced in the deterioration of polarizing performance under high-temperature and high-humidity conditions, namely, excellent in the durability, which is composed of an obliquely stretched polarizing film capable of improving the yield in  
25 the step of punching the polarizing plate.

Still another object of the present invention is to provide a production method using an oblique stretching method, where the above-described polarizing plate having excellent dimensional stability can be easily produced, and  
5 to provide a liquid crystal display including the above-described polarizing plate.

These objects can be attained by the following constitutions.

10 1. A polarizing plate comprising:  
a polarizing film; and  
a protective film attached to at least one surface of the polarizing film,

wherein the angle made by the stretching axis of the  
15 protective film and the stretching axis of the polarizing film is no less than  $10^\circ$  and less than  $90^\circ$ .

2. The polarizing plate as described in the item 1, which is a long polarizing plate in a roll-form, wherein  
20 the protective film having a stretching axis in parallel to the longitudinal direction is attached to at least one surface of the polarizing film having a stretching axis neither in parallel nor perpendicular to the longitudinal direction.

25

3. A long polarizing film having:  
an absorption axis neither in parallel nor  
perpendicular to the longitudinal direction;  
a polarization degree of 90% or more at 550 nm;  
5 a single plate transmittance of 35% or more at 550  
nm; and  
a dispersion of an angle of the stretching axis to  
the longitudinal direction of within  $\pm 0.5^\circ$ , when the angle  
is measured in the cross direction.
- 10
4. A long polarizing film having:  
an absorption axis neither in parallel nor  
perpendicular to the longitudinal direction;  
a polarization degree of 90% or more at 550 nm;  
15 a single plate transmittance of 35% or more at 550  
nm;  
a dispersion of the in-plane polarization degree of  
within  $\pm 0.5\%$ ; and  
a dispersion of the single plate transmittance of  
20 within  $\pm 0.5\%$ .
5. A long polarizing film having:  
an absorption axis neither in parallel nor  
perpendicular to the longitudinal direction;  
25 a polarization degree of 80% or more at 550 nm;

a single plate transmittance of 35% or more at 550 nm; and

a surface roughness: Ra of 10  $\mu\text{m}$  or less.

5           6. The polarizing plate as described in the item 2, wherein

(a) the polarizing film has an absorption axis neither in parallel nor perpendicular to the longitudinal direction,

10           the polarizing plate has a single plate transmittance of 40% or more at 550 nm and a polarization degree of 95% or more at 550 nm, when the polarization degree is calculated by formula (1) below, and

(b) when the polarizing plate is left standing in  
15 an atmosphere at a temperature of 60°C and a humidity of 90% for 500 hours, the polarizing plate has:

(b-1) a fluctuation width of the transmittance at 550 nm of within  $\pm 10\%$ , as compared with the initial value; and

(b-2) a fluctuation width of the polarization degree  
20 at 550 nm of within  $\pm 10\%$ , as compared with the initial value:

Formula (1)

$$P = [(H_0 - H_1) / (H_0 + H_1)]^{1/2} \times 100$$

wherein  $H_0$  is a transmittance (%) when two polarizing  
25 plates are superposed so that the absorption axes are

agreed, and H1 is a transmittance (%) when two polarizing plates are superposed so that the absorption axes are orthogonalized.

5           7.     The long polarizing film as described in the item 5, wherein the number of color slippage streaks is 4 or less per 1 m<sup>2</sup>.

          8.     The polarizing plate as described in the item 1,  
10   2 or 6, wherein the protective film is a transparent film and the retardation of the polarizing plate at 632.8 nm is 10 nm or less.

          9.     A method for producing a polarizing plate,  
15   comprising attaching a stretched protective film in a roll-form to at least one surface of a polarizing film,

          wherein the polarizing film is produced by a method for stretching a polymer film, comprising:

          holding both edges of a continuously fed  
20   polymer film by holding means; and

          stretching the film, while travelling said holding means to the longitudinal direction of the film and applying tension to the film,

          wherein, when L1 represents a trajectory of the  
25   holding means from a substantial holding start point

until a substantial holding release point at one edge of the polymer film, L2 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at the other edge of the polymer film, and W represent a distance between the two substantial holding release points, L1, L2 and W satisfy a relation represented by formula (2) below, and the difference in the conveyance speed in the longitudinal direction between right and left film gripping means is less than 1%:

Formula (2)

$$|L2-L1| > 0.4W$$

10. The method for producing a polarizing plate as described in the item 9, wherein the polymer film is stretched while keeping the supporting property of the polymer film and allowing a volatile content ratio of 5% or more to be present, and then is shrunk while reducing the volatile content ratio.

11. The method for producing a polarizing plate as described in the item 9, wherein the polymer film for the polarizing film is a polyvinyl alcohol-base film.

12. The method for producing a polarizing plate as described in the item 10, wherein, when the polymer film is shrunk while reducing the volatile content ratio, a reduction rate of the volatile content ratio is 1%/min.

5

13. The method for producing a polarizing plate as described in any one of items 9 to 12, wherein an angle made by the longitudinal direction and the absorption axis direction of the polarizing film is from 20 to 70°.

10

14. The method for producing a polarizing plate as described in the item 13, wherein the angle made by the longitudinal direction and the absorption axis direction of the polarizing film is from 40 to 50°.

15

15. The method for producing a polarizing plate as described in any one of items 9 to 14, which comprises:

drying the stretched polymer film for the polarizing film to shrink and reduce the volatile content ratio;

20

attaching the protective film to at least one surface of the polymer film after or during the drying; and

heat-treating the laminate of the protective film and the polymer film.

25

16. A method for producing a polarizing plate,

comprising attaching a stretched protective film in a roll-form to at least one surface of a polarizing film, the polarizing film having:

a polarization degree of 80% or more at 550 nm;

5 a single plate transmittance of 35% or more at 550 nm; and

a surface roughness: Ra of 10  $\mu$ m or less,

wherein the polarizing film is produced by a method for stretching a polymer film, comprising:

10 holding both edges of a continuously fed polymer film by holding means; and

stretching the film while travelling said holding means to the longitudinal direction of the film, and while applying tension to the film;

15 wherein, when L1 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at one edge of the polymer film, L2 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at  
20 the other edge of the polymer film, and W represent a distance between the two substantial holding release points, L1, L2 and W satisfy a relation represented by formula (2):  $|L2-L1| > 0.4W$ ,

25 the polymer film for the polarizing film has an



elastic modulus of from 0.1 to 500 MPa before stretching, and

the polymer film is stretched while keeping the supporting property of the polymer film, and while  
5 allowing a volatile content ratio of 5% or more to be present, and then is shrunk while reducing the volatile content ratio.

17. The method for producing a polarizing plate as  
10 described in the item 16, wherein the polymer film for the polarizing film is a film of a polyvinyl alcohol having a number average polymerization degree of 2,000 to 5,000.

18. The method for producing a polarizing plate as  
15 described in the item 16, wherein the method for stretching the polymer film for the polarizing film comprises a step of adding a metal salt.

19. The method for producing a polarizing plate as  
20 described in the item 18, wherein the step of adding a metal salt is a step of dipping the polymer film in a solution containing a metal salt.

20. The method for producing a polarizing plate as  
25 described in the item 19, wherein a metal salt

concentration in the solution containing a metal salt is from 0.01 to 10.0 wt%.

21. The method for producing a polarizing plate as  
5 described in any one of items 9 to 15, wherein the distribution of the volatile component content in the film for the polarizing film is 5% or less before stretching.

22. The method for producing a polarizing plate as  
10 described in the item 16, wherein, after attaching a stretched protective film in a roll-form to at least one surface of the polarizing film, the laminate of the polarizing film and the protective film is subjected to an after-heating.

15

23. A liquid crystal display comprising a liquid crystal cell and polarizing plates disposed in both sides of the liquid crystal cell,

wherein at least one of the polarizing plates is a  
20 polarizing plate punched out from at least one selecting from the group consisting of:

the polarizing plate described in items 1, 2 or 6;

a polarizing plate having at least one of the polarizing films described in items 3, 4, 5 and 7; and

25 a polarizing plate produced by the method described

in any one of items 9 to 22.

#### Brief Description of the Drawings

Fig. 1 is a schematic perspective view showing the  
5 polarizing plate of the present invention.

Fig. 2 is a schematic plan view showing the state of  
punching the polarizing plate of the present invention.

Fig. 3 is a schematic plan view showing one example  
of the method for obliquely stretching a polymer film of  
10 the present invention.

Fig. 4 is a schematic plan view showing one example  
of the method for obliquely stretching a polymer film of  
the present invention.

Fig. 5 is a schematic plan view showing one example  
15 of the method for obliquely stretching a polymer film of  
the present invention.

Fig. 6 is a schematic plan view showing one example  
of the method for obliquely stretching a polymer film of  
the present invention.

20 Fig. 7 is a schematic plan view showing one example  
of the method for obliquely stretching a polymer film of  
the present invention.

Fig. 8 is a schematic plan view showing one example  
of the method for obliquely stretching a polymer film of  
25 the present invention.

Fig. 9 is a schematic plan view showing the layer structure of the liquid crystal display of Examples.

Fig. 10 is a schematic view showing the relationship between the stretching axis of the protective film and the stretching axis of the polarizing film in Examples.

Fig. 11 is a schematic plan view showing the state of punching a conventional polarizing plate.

Fig. 12 is a schematic conceptual view of an air blow device.

Fig. 13 is a schematic conceptual view of a nip device.

Fig. 14 is a schematic conceptual view of a blade device.

The reference numbers in the figure are as follows.

(i) direction of introducing film

(ii) direction of conveying film to next step

(a) step of introducing film

(b) step of stretching film

(c) step of delivering stretched film to next step

A1 position of engaging film with holding means and position of starting stretching film (substantial holding start point: right)

B1 position of engaging film with holding means (left)

C1 position of starting stretching film  
(substantial holding start point: left)

Cx position of releasing film and final basis  
position of film stretching (substantial holding release  
5 point: left)

Ay final basis position of film stretching  
(substantial holding release point: right)

|L1-L2| difference in pathway between right and  
left film holding means

10 W substantial width at the end of film stretching  
step

$\theta$  angle made by stretching direction and film-  
travelling direction

11 center line of film in the introduction side

15 12 center line of film delivered to next step

13 trajectory of film holding means (left)

14 trajectory of film holding means (right)

15 film in the introduction side

16 film delivered to next step

20 17, 17' left and right points of starting holding  
(engaging) film

18, 18' left and right points of releasing film  
from holding means

21 center line of film in the introduction side

25 22 center line of film delivered to next step

- 23 trajectory of film holding means (left)
- 24 trajectory of film holding means (right)
- 25 film in the introduction side
- 26 film delivered to next step
- 5 27, 27' left and right points of starting holding  
(engaging) film
- 28, 28' left and right points of releasing film  
from holding means
- 33, 43, 53, 63 trajectory of film holding means  
10 (left)
- 34, 44, 54, 64 trajectory of film holding means  
(right)
- 35, 45, 55, 65 film in the introduction side
- 36, 46, 56, 66 film delivered to next step
- 15 70 a protective film
- 71, 71' stretching axis (phase lag axis) of  
protective film
- 74 adhesive layer
- 80 polarizing film
- 20 81 stretching axis (absorption axis) of polarizing  
film
- 72, 82 longitudinal direction
- 83 transverse direction
- 90 polarizing plate
- 25 91, 92 iodine-type polarizing plate

- 97 liquid crystal cell
- 98 backlight
- 101 air blow device
- 111 nip device
- 5 121 blade device

That is, it has been found that when a stretched protective film and a stretched polarizing film are combined such that the stretching axes make an angle of no less than 10 and less than 90°, the dimensional stability is remarkably improved and excellent aging stability can also be obtained. More specifically, Fig. 1 shows a polarizing plate 90 obtained by attaching a protective film 70 having a stretching axis 71 to at least one surface of a polarizing film 80 having a stretching axis 81, if desired, through an adhesive layer 75, wherein the angle  $\theta$  between the stretching axis 81 of the polarizing film and the stretching axis 71 (namely, dotted line 71') of the protective film is no less than 10 and less than 90°. Within this range, an excellent dimensional stability can be obtained. In view of the dimensional stability and polarizing performance, the angle between the stretching axes of the protective film and the polarizing film is preferably from 20 to 80°, more preferably from 40 to 50°.

The polarizing plate as used herein includes not only

a lengthy polarizing plate in a roll form but also a polarizing plate punched out for LCD from the lengthy polarizing plate. With respect to the angle between the stretching axis of the polarizing plate and the stretching axis of the protective film, when the protective film and the polarizing film of the polarizing plate are peeled off and the absorption axis of the polarizing plate and the phase lag axis of the protective film are measured, the angle made by the absorption axis and the phase lag axis can be estimated.

The stretching axis of the polarizing film is defined as the axis direction of giving a maximum transmission density when the polarizing plate is superposed on a polarizing plate having a known absorption axis in the cross nicol state. The stretching axis of the protective film is defined as the axis direction of giving a maximum refractive index when the refractive index in plane of the protective film is measured. The angle between the stretching axis of the polarizing film and the stretching axis of the protective film means an angle made by those axis directions. In the present invention, this angle is no less than 10 and less than 90°. The transmission density of the polarizing film can be measured by a transmission densitometer (for example, X Rite. 310TR having mounted thereon a status M filter) and the



refractive index of the protective film can be measured by an ellipsometer (for example, AEP-10, manufactured by Shimadzu Corporation).

It is preferred that the stretching axis 71 of the protective film 70 runs in parallel to the longitudinal direction 82 or transverse direction 83 of the polarizing plate and the stretching axis 81 of the polarizing film 80 makes an angle of  $45^\circ$  with respect to the longitudinal direction 82 or transverse direction 83 of the polarizing plate.

The preparation of the stretched protective film for use in the present invention includes not only the case of stretching the film by providing a stretching step but also the case where an independent stretching step is not provided and the film is stretched by the tension additionally imposed in the longitudinal direction of roll in the after-heating step after the drying of film for the protective film.

The polarizing plate can be easily obtained by designing the polarizing film and the protective film each having a stretching axis to give the above-described angle of stretching axes and combining these films. However, it is preferred to use a roll-form polarizing plate where, as shown in Fig. 2, a protective film having a stretching axis 71 in parallel to the longitudinal direction is attached to

at least one surface of a polarizing film having a stretching axis 81 which is neither parallel nor perpendicular to the longitudinal direction 82 (namely, obliquely oriented polarizing film). By this, when the polarizing plate is punched as shown in Fig. 2, the yield in the step of punching the polarizing plate can be improved.

The polarizing film obliquely oriented as shown in Fig. 2 can be produced by a method of holding both edges of a continuously fed polymer film and stretching the film by applying a tension while allowing the holding means to proceed in the longitudinal direction of film, wherein the trajectory L1 of the holding means from the substantial holding start point at one end of the polymer film until the substantial holding release point, the trajectory L2 of the holding means from the substantial holding start point at another end of the polymer film until the substantial holding release point and the distance W between two substantial holding release points satisfy the following formula (1) and the difference of the transportation speed in the longitudinal direction of the left and right film gripping means is less than 1% (hereinafter, this method is especially called a specific oblique stretching method). On at least one surface of the obliquely stretched polarizing film obtained as such, a roll-form protective

film having a stretching axis in the longitudinal direction is continuously attached, whereby a roll-form polarizing plate can be more efficiently produced.

Fig. 11 shows an example of punching a conventional polarizing plate. In the conventional polarizing plate, as shown in Fig. 11, the absorption axis 71 of polarization, namely, the stretching axis agrees with the longitudinal direction 72, whereas in the polarizing plate of the present invention, as shown in Fig. 2, the absorption axis 81 of polarization, namely, the stretching axis is inclined at 45° with respect to the longitudinal direction 82 and this angle agrees with the angle made, when attached with a liquid crystal cell in LCD, between the absorption axis of the polarizing plate and the vertical or transverse direction of the liquid crystal cell itself, therefore, oblique punching is not necessary in the punching step. Moreover, as seen from Fig. 2, since the polarizing plate of the present invention is cut in a straight line along the longitudinal direction, a practical polarizing plate can also be produced without punching the lengthy polarizing plate but by slitting it along the longitudinal direction, as a result, remarkably high productivity is attained.

The polarizing plate of the present invention comprises a polarizing film having a polarizing ability and

on both surfaces or one surface of the polarizing film, a protective film is usually provided through an adhesive layer. In general, a lengthy polarizing plate (usually in a roll form) is produced and punched according to use, 5 whereby a practical polarizing plate is obtained. Unless otherwise indicated, the "polarizing plate" as used in the present invention includes both a lengthy polarizing plate and a punched polarizing plate.

The polarizing film of a first preferable embodiment 10 of the present invention is as described above characterized in that in a long polarizing plate (a lengthy polarizing plate), the absorption axis is neither in parallel nor perpendicular to the longitudinal direction (hereinafter, this lengthy polarizing plate is sometimes 15 simply referred to as an "obliquely oriented" polarizing plate). The tilt angle between the longitudinal direction and the absorption axis direction is preferably from  $10^\circ$  to less than  $90^\circ$ , more preferably from  $20^\circ$  to  $70^\circ$ , still more preferably from  $40^\circ$  to  $50^\circ$ , particularly preferably from  $44^\circ$  20 to  $46^\circ$ . With this tilt angle, a single polarizing plate can be obtained in a high yield in the step of punching it from the lengthy polarizing plate.

In the present invention, the tilt angle can be freely set. Accordingly, an optimal angle can be freely 25 selected when the polarizing plate is used by combining it

with other optical member.

The polarizing film of a first preferable embodiment of the present invention is also characterized in that the single plate transmittance is 35% or more at 550 nm and the polarization degree is 90% or more at 550 nm. The single plate transmittance is preferably 40% or more and the polarization degree is preferably 95.0% or more, more preferably 99% or more, particularly preferably 99.9% or more. The polarizing plate of the present invention has excellent single plate transmittance and polarization degree and therefore, when used as a liquid crystal display, the contrast can be advantageously elevated.

The obliquely oriented polarizing plate of the present invention can be easily obtained by the method described below. That is, oblique orientation is obtained by the stretching of a polymer film and at the same time, the volatile content ratio at the stretching of film, the shrinkage percentage at the shrinking of film, and the elastic modulus of film before stretching are designed. It is also preferred to control the amount of foreign matters adhering to the film before stretching.

In the polarizing film of a first preferable embodiment of the present invention, the dispersion of angle of the stretching axis with respect to the longitudinal direction, measured in the cross direction, is

small, specifically, the dispersion is within  $\pm 5^\circ$ , preferably  $\pm 3^\circ$ . As a result, the dispersion of the black part density at the cross nicol time is actually eliminated and the grade is elevated.

5        The width in the above-described cross direction means a width effective as a polarizing film (effective width) excluding the holding portion at both edges, and the like at the preparation of the polarizing film.

10        In order to reduce the dispersion of stretching axis, after the stretching to a desired tilt angle, the orientation state is swiftly fixed. As the effective means for this purpose, a method of controlling the volatile content ratio at the stretching of the polymer film, the shrinkage percentage at the shrinking of the film, the  
15        drying point of the film and the reduction rate of the volatile content ratio are used.

20        In the polarizing film of a second preferable embodiment of the present invention, the dispersion of polarization degree and transmittance (the ratio of a difference between the maximum value or minimum value for the average value of the polarization degree and transmission in plane, and the average value) can be reduced by controlling the volatile content ratio at the stretching of film, the shrinkage percentage at the  
25        shrinking of film, the amount of foreign matters adhering

to film before stretching, the volatile content ratio reduction rate, and the distribution of the volatile component content in the film before stretching.

The polarizing plate of a third preferable embodiment  
5 of the present invention is also characterized in that the surface roughness  $R_a$  of the polarizing film is 10  $\mu\text{m}$  or less. The surface roughness  $R_a$  of the polarizing film is preferably 5  $\mu\text{m}$  or less, more preferably 1  $\mu\text{m}$  or less. The surface roughness  $R_a$  used here indicates a value measured  
10 by the standard and measuring method described in JIS B0601 and B0660. In practice, the surface roughness can be measured by a general device such as roughness meter and AFM.

In the present invention, the surface roughness  $R_a$  of  
15 the obliquely oriented polarizing film is 10  $\mu\text{m}$  or less, whereby an excellent polarizing plate free from the generation of color slippage streaks can be obtained. Namely, the present invention provides a polarizing plate having 4 or less color slippage streaks per 1  $\text{m}^2$ . The  
20 color slippage streak as used herein means streak-like color change observed on a polarizing film or a polarizing plate. The color slippage streak is confirmed with an eye and specifically indicates a part in a length of 1 cm or more and a width of 0.1 cm or more and having a difference  
25 of 0.2 or more in the density at 550 nm from the normal

part. The number of color slippage streaks is preferably 4 streaks or less, more preferably 2 streaks or less, still more preferably one streak or less, per 1 m<sup>2</sup> of the polarizing plate.

5       The polarizing film of a third preferable embodiment of the present invention is furthermore characterized in that the single plate transmittance is 35% or more at 550 nm and the polarization degree is 80% or more at 550 nm. The single plate transmittance is preferably 40% or more  
10 and the polarization degree is preferably 95.0% or more, more preferably 99% or more, particularly preferably 99.9% or more. In the present invention, unless otherwise indicated, the transmittance means a single plate transmittance. The polarizing plate of the present  
15 invention has excellent single plate transmittance and polarization degree and therefore, when used as a liquid crystal display, the contrast can be advantageously elevated.

20       The obliquely oriented polarizing plate of the present invention can be easily obtained by the method described below. That is, oblique orientation is obtained by the stretching of a polymer film and at the same time, the volatile content ratio at the stretching of film, the shrinkage percentage at the shrinking of film, and the  
25 elastic modulus of film before stretching are designed. It



is also preferred to control the amount of foreign matters adhering to the film before stretching. By these, a polarizing film having a small surface roughness and excellent smoothness and free from wrinkling and drawing  
5 even when obliquely stretched can be obtained. Since wrinkling/drawing is not generated, warping does not occur and the stretching tension applied to the film is not decreased. This is presumed be a reason for no generation of streaky color change.

10 The polarizing plate of a preferable embodiment of the present invention has excellent durability, namely, is reduced in the fluctuation of polarizing performance under high-temperature high-humidity conditions. Moreover, a polarizing plate as long as 10 m or more and having  
15 excellent durability can be manufactured in a roll form for the first time in the present invention. As a result, the polarizing plate can be roll-to-roll attached with another optical member, for example,  $\lambda/4$  plate and the productivity is elevated. By virtue of the roll form, this polarizing  
20 plate is also excellent in the packing property and storability. Furthermore, a polarizing plate for a liquid crystal display can be punched from the roll-form polarizing plate in a high yield.

The polarizing plate of a preferable embodiment of  
25 the present invention is also characterized in that the

single plate transmittance is 40% or more at 550 nm and the polarization degree calculated by formula (1) is 95% or more at 550 nm. The single plate transmittance is preferably 40% or more, more preferably 43% or more and the  
5 polarization degree is preferably 99% or more, more preferably 99.9% or more. In the present invention, unless otherwise indicated, the transmittance means a single plate transmittance.

The polarizing plate of a preferable embodiment of  
10 the present invention has excellent single plate transmittance and polarization degree and therefore, when used as a liquid crystal display, the contrast can be advantageously elevated.

Furthermore, the polarizing plate of a preferable  
15 embodiment of the present invention is characterized in that when measured after allowing the polarizing plate to stand in an atmosphere at a temperature of 60°C and a humidity of 90% for 500 hours, the fluctuation width of the transmittance at 550 nm is within  $\pm 10\%$  as compared with the  
20 initial value and the fluctuation width of the polarization degree at 550 nm is within  $\pm 10\%$  as compared with the initial value. As such, the polarizing plate of the present invention is prevented from deterioration in the polarizing performance under high-temperature high-humidity  
25 conditions and exhibits excellent durability.

The initial value as used herein means a value before the polarizing plate is exposed to a high-temperature high-humidity environment.

The obliquely oriented polarizing plate of the present invention can be easily obtained by the method described below. That is, oblique orientation is obtained by the stretching of a polymer film and at the same time, the volatile content ratio at the stretching of film, the addition of a metal salt to the film, and the polymerization degree of the polymer constituting the film are designed. It is also preferred to control the amount of foreign matters adhering to the film before stretching.

#### <Durability>

When a liquid crystal display is used outdoors for a long period of time, there arise problems of deterioration, such as decrease or increase in the transmittance of the display picture plane, color change such as decoloration or discoloration, and reduction in the polarization degree.

When a polarizing plate is left standing in an atmosphere at a temperature of 60°C and a humidity of 90%, a phenomenon such that the support undergoes heat shrinkage and the polarizing film and the protective film deteriorate takes place. This can be used as a test of promoting the deterioration of a polarizing plate. In view of resistance against heat and against humidity and heat, the polarizing

plate of the present invention is preferably small in the fluctuation width of transmittance and polarization degree in the above-described deterioration promoting test. More specifically, after the polarizing plate is left standing  
5 in an atmosphere at a temperature of 60°C and a humidity of 90% for 500 hours, the fluctuation width of transmittance is within  $\pm 10\%$ , preferably  $\pm 5\%$ , more preferably  $\pm 2\%$ , as compared with the initial value and the fluctuation width of the polarization degree is  $\pm 10\%$ , preferably  $\pm 5\%$ , more  
10 preferably  $\pm 2\%$ , as compared with the initial value.

The polarizing plate of the present invention can be made to have such durability by a method where a film comprising a polymer having a number average polymerization degree of 1,000 to 10,000, preferably from 2,000 to 5,000  
15 is used as the polymer film for the polarizing film and a metal salt is incorporated into the polarizing film. However, the present invention is not limited to this method.

In the polarizing plate of the present invention, a  
20 protective film is attached to at least one surface of the polarizing film such that the tilt angle between the stretching axis of the protective film and the stretching axis of the polarizing film becomes no less than 10 and less than 90°. As long as this requirement is satisfied,  
25 the method of attaching the combining these is not

particularly limited. The adhesive for combining the polarizing film and the protective film is not particularly limited and examples thereof include PVA-base resin (including modified PVA such as acetoacetyl group, sulfonic acid group, carboxyl group and oxyalkylene group) and an aqueous solution of boron compound. Among these, PVA-base resin is preferred. The thickness of the adhesive layer after drying is preferably from 0.01 to 10  $\mu\text{m}$ , more preferably from 0.05 to 5  $\mu\text{m}$ .

10           Examples of the method for combining these films include a method where a normal polarizing film stretched in the longitudinal direction and a protective film each is punched and these punched films are combined such that respective stretching axes make the above-described tilt angle. At least either one of the polarizing film and the protective film preferably has a stretching axis which is neither in parallel nor perpendicular to the longitudinal direction, because the polarizing plate of the present invention where the tilt angle made by the stretching axes is not parallel can be obtained without previously punching the polarizing plate and the protective film but only by attaching the protective film and the polarizing film each in a roll form.

25           In particular, the polarizing film preferably has a stretching axis neither in parallel nor perpendicular to

the longitudinal direction. Furthermore, the polarizing film used as the polarizing plate for LCD preferably has a stretching axis inclined at an angle of 40 to 50°, more preferably from 44 to 46°, with respect to the longitudinal direction.

The polarizing film having a stretching axis neither in parallel nor perpendicular to the longitudinal direction is preferably produced, as described above, by a specific oblique stretching method. This method is described in detail below.

Figs. 3 and 4 each is a schematic plan view showing a typical example of the method for obliquely stretching a polymer film.

The specific oblique stretching method comprises (a) a step of introducing an original film in the direction of the arrow (i), (b) a step of stretching the film in the transverse direction, and (c) a step of conveying the stretched film to the next step, namely, in the direction of the arrow (ii). The "stretching step" referred to hereinafter contains these steps (a) to (c) and indicates the entire step for performing the oblique stretching method.

The film is continuously introduced from the direction (i) and first held at the point B1 by the holding means in the left side seen from upstream. At this point,

the other edge of the film is not held and tension is not generated in the cross direction. In other words, the point B1 is not a point where the holding is substantially started (hereinafter referred to as a "substantial holding  
5 start point").

The substantial holding start point is defined as the point where both edges of the film are first held. The substantial holding start point includes two points, that is, a holding start point A1 in the more downstream side  
10 and a point C1 where a straight line drawn almost perpendicularly to the center line 11 (Fig. 3) or 21 (Fig. 4) of the film in the side of introduction from A1 meets the trajectory 13 (Fig. 3) or 23 (Fig. 4) of the holding means in the opposite side.

15 Starting from these points, when the film is conveyed by the holding means at both edges at a substantially equal speed, A1 moves to A2, A3 ... An every each unit time and C1 similarly moves to C2, C3 ... Cn. That is, the straight line connecting points An and Cn where the holding  
20 means as the bases pass at the same time is the stretching direction at that time.

In the specific oblique stretching method, as shown in Figs. 3 and 4, An is gradually delayed from Cn and therefore, the stretching direction is gradually inclined  
25 from the direction perpendicular to the conveyance

direction. The point of substantially releasing the holding (hereinafter referred to as a "substantial holding release point") is defined by two points, that is, a point Cx where the film leaves the holding means in the more upstream side, and a point Ay where a straight line drawn almost perpendicularly to the center line 12 (Fig. 3) or 22 (Fig. 4) of the film delivered to the next step from Cx meets the trajectory 14 (Fig. 3) or 24 (Fig. 4) of the holding means in the opposite side.

The angle of the final stretching direction of the film is determined by the ratio of the pathway difference between the right and left holding means at the substantial end point of the stretching step (substantial holding release point),  $Ay - Ax$  (that is,  $|L1 - L2|$ ), to the distance W between substantial holding release points (distance between Cx and Ay). Accordingly, the tilt angle  $\theta$  of the stretching direction with respect to the conveyance direction to the next step is an angle satisfying the relationship:

$$\tan\theta = W/(Ay - Ax), \text{ that is,}$$

$$\tan\theta = W/|L1 - L2|$$

The film edge in the upper side of Figs. 3 and 4 is held until 18 (Fig. 3) or 28 (Fig. 4) even after the point Ay, however, since the other edge is not held, the stretching in the cross direction is not newly generated.



Therefore, 18 and 28 are not a substantial holding release point.

As in the above, the substantial holding start points present at both edges of the film are not a point where the  
5 film is merely engaged with each of right and left holding means. To more strictly describe the two substantial holding start points defined above, these are defined as points where a straight line connecting the left or right  
holding point and another holding point almost  
10 perpendicularly meets the center line of the film introduced into the step of holding the film, and which are two holding points positioned most upstream.

Similarly, the two substantial holding release points are defined as points where a straight line connecting the  
15 left or right holding point and another holding point almost perpendicularly meets the center line of the film delivered to the next step, and which are two holding points positioned most downstream.

The term "almost perpendicularly meet" as used herein  
20 means that the center line of the film makes an angle of  $90 \pm 0.5^\circ$  with the straight line connecting the left and right substantial holding start points or substantial holding release points.

In the case of giving a difference between the left  
25 and right pathways by using a tenter-system stretching

machine, due to the mechanical limitation such as rail length, there arises a large dislocation between the point of being engaged with the holding means and the substantial holding start point or between the point of being disengaged from the holding means and the substantial holding release point, however, as long as the pathway from the substantial holding start point to the substantial holding release point defined above satisfies the relationship in formula (1), the oblique stretching can be effectively performed.

The tilt angle of the orientation axis of the stretched film obtained can be controlled and adjusted by the ratio of the outlet width  $W$  in the step (c) to the substantial difference in the pathway between the right and left holding means  $|L1-L2|$ .

For the polarizing plate and phase difference film, a film oriented at  $45^\circ$  with respect to the longitudinal direction is often required. In this case, for obtaining an orientation angle close to  $45^\circ$ , the following formula (2) is preferably satisfied:

$$\text{Formula (2): } 0.9W < |L1-L2| < 1.1W,$$

More preferably, the following (3) is satisfied:

$$\text{Formula (3): } 0.97W < |L1-L2| < 1.03W.$$

Specific examples of the stretching step are shown in

Figs 1 to 6 where the polymer film is obliquely stretched while satisfying formula (1), and these can be freely designed by taking account of the equipment cost and productivity.

5           The angle made by the direction (i) of introducing the film into the stretching step and the direction (ii) of conveying the film to the next step may have an arbitrary numerical value, however, from the standpoint of minimizing the total installation area for the equipment including the  
10 steps before and after the stretching, this angle is preferably smaller and is preferably  $3^\circ$  or less, more preferably  $0.5^\circ$  or less. This value can be achieved, for example, by the structure shown in Figs. 3 and 6.

          In such a method where the film travelling direction  
15 is substantially not changed, the orientation angle of  $45^\circ$  with respect to the longitudinal direction, which is preferred as a polarizing plate or phase difference film, can be difficultly obtained only by the enlargement of the width of the holding means. As in Fig. 3, by providing a  
20 step of shrinking the film after the film is once stretched,  $|L1-L2|$  can be made large.

          The stretching ratio is preferably from 1.1 to 10.0 times, more preferably from 2 to 10 times. The shrinkage percentage at the subsequent shrinking step is preferably  
25 10% or more. Furthermore, as shown in Fig. 6, the

stretching-shrinking is also preferably repeated a plurality of times because  $|L1-L2|$  can be made large.

From the standpoint of minimizing the equipment cost in the stretching step, the number of turns in the trajectory of the holding means and the angle of bending are preferably smaller. In this viewpoint, as shown in Figs. 4, 5 and 7, the film travelling direction is preferably bent while keeping the state of holding both edges of the film, so that the angle made by the film travelling direction at the outlet of the step of holding both edges of the film and the substantial stretching direction of the film can be inclined at 20 to 70°.

The device for stretching the film by applying tension while holding both edges is preferably a so-called tenter device as shown in Figs. 3 to 7. Other than the conventional two-dimensional tenter, a stretching step where, as shown in Fig. 8, a difference is spirally given between the pathways of the gripping means at both edges may also be used.

In many cases, the tenter-type stretching machine has a structure where a clip-fixed chain runs along the rail. However, when a vertically non-uniform stretching method as in the present invention is employed, the end terminal of one rail may dislocate, as shown in Figs. 3 and 4, from the end terminal of another rail at the inlet and outlet of the

step and engaging or disengaging may not occur simultaneously at left and right edges. In this case, the substantial pathway lengths L1 and L2 are not a simple engaging-to-disengaging distance but, as already described  
5 above, a length of pathway where the holding means hold both edges of the film.

If the film travelling speed is different between left and right edges at the outlet of the stretching step, wrinkling or slippage occurs. Therefore, right and left  
10 film gripping means are demanded to convey the film at a substantially the same speed. The difference in the speed is preferably 1% or less, more preferably less than 0.5%, most preferably less than 0.05%. The speed as used herein means the length of trajectory which each of left and right  
15 holding means proceeds per minute. In a general tenter stretching machine or the like, according to the cycle of sprocket wheel driving the chain, the frequency of driving motor and the like, unevenness in the order of seconds or less is generated in the speed and unevenness of a few % is  
20 often generated, however, these do not come under the difference in the speed referred to in the present invention.

As the right and left pathways come to differ, wrinkling or slippage of film is generated. In order to  
25 solve these problems, the polymer film is preferably

stretched while keeping the supporting property and allowing 5% or more of volatile content to be present, and then shrunk to reduce the volatile content. The term "polymer film keeps the supporting property" as used herein  
5 means that the film is held at both sides without impairing the film property.

Furthermore, "stretched while allowing 5% or more of volatile content to be present" does not necessarily mean that the volatile content ratio of 5% or more is maintained  
10 throughout the process in the stretching step, but as long as the stretching at a volatile content ratio of 5% or more exerts the effect of the present invention, the volatile content ratio may be 5% or less in a part of the step. Examples of the method for incorporating a volatile content  
15 in such a form include a method of casting a film and then incorporating a volatile content such as water or a non-aqueous solvent, dipping, coating or spraying the film in or with a volatile content such as water or a non-aqueous solvent before stretching, or coating a volatile content  
20 such as water or a non-aqueous solvent during the stretching. The hydrophilic polymer such as polyvinyl alcohol contains water in a high-temperature and high-humidity atmosphere and therefore, by conditioning the humidity in a high-humidity atmosphere and then stretching  
25 the film or by stretching the film under high-humidity

conditions, the volatile content can be incorporated. Other than these methods, any means may be used if the volatile content of the polymer film can be made 5% or more.

The preferred volatile content ratio varies depending  
5 on the kind of the polymer film. The maximum of the volatile content ratio may be any as long as the polymer film can keep the supporting property. The volatile content ratio is preferably from 10 to 100% for polyvinyl alcohol and preferably from 10 to 200% for cellulose  
10 acylate.

<Shrinkage Percentage: shrinkage percentage during or after stretching>

The shrinking of the stretched polymer film may be performed in either step during or after stretching. It  
15 may suffice if the wrinkling of polymer film and the dispersion of stretching axis generated at the orientation in the oblique direction are eliminated by the shrinking. For shrinking the film, a method of heating the film and thereby removing the volatile content may be used, however,  
20 any means may be used if it can shrink the film. The film is preferably shrunk to  $1/\sin\theta$  or more times, where  $\theta$  is an orientation angle with respect to the longitudinal direction. The shrinkage percentage is preferably 10% or more.

## &lt;Distance from Generation of Wrinkling to Disappearance&gt;

The wrinkling of polymer film, generated at the orientation in the oblique direction, may be sufficient if it disappears until the substantial holding release point in the present invention. However, if a long time is spent from the generation of wrinkling to the disappearance, dispersion may be generated in the stretching direction. Therefore, the wrinkling preferably disappears in a travelling distance as short as possible from the point where the wrinkling is generated. For this purpose, for example, a method of increasing the volatilization speed of the volatile content may be used.

## &lt;Distribution of Volatile Component Content&gt;

In the case of manufacturing a lengthy, particularly roll-form polarizing plate by a through step, it is necessary that uneven dyeing or non-dyed spot is not present. If the volatile component in the film before the stretching has an uneven distribution (difference in the volatile component amount depending on the site in the film plane), this causes uneven dyeing or non-dyed spot. Accordingly, the distribution of the volatile component content in the film before stretching is preferably smaller and this is preferably at least 5% or less. The volatile content ratio as used in the present invention means a volume of volatile component contained per the unit volume



of film and is a value obtained by dividing the volatile component volume by the film volume. The distribution thereof means a fluctuation width of the volatile content ratio per 1 m<sup>2</sup> (a ratio of a larger difference out of differences between the maximum value or minimum value and the average volatile content ratio, to the average volatile content ratio). For reducing the distribution of the volatile component content, a method of blowing the front and back surfaces of the film by a uniform air, a method of uniformly squeezing the film by nip rollers, or a method of wiping off the volatile component by a wiper may be used, however, any method may be used insofar as the distribution can be uniform.

Figs. 12 to 14 show one example of an air blow device, a nip device and a blade device, respectively.

#### <Elastic Modulus>

As for the physical properties of the polymer film before stretching, if the elastic modulus is too low, the shrinkage percentage during or after stretching decreases and the wrinkling difficultly disappears, whereas if it is excessively high, a great tension is applied at the stretching, as a result, the portion of holding both edges of the film must be increased in the strength and a load on the machine increases. The elastic modulus of film is preferably, in terms of Young's modulus, from 0.01 to

5,000 MPa, more preferably from 0.1 to 500 MPa.

<Drying: drying speed and drying point>

In order to manufacture a lengthy, particularly roll-form polarizing plate, a protective film must be attached in the state where the volatile content is decreased. The polymer film is preferably dried before attaching the protective film and preferably has a drying point before releasing the holding of both edges. More preferably, the drying point is adjusted to come in a traveling distance as short as possible after a desired orientation angle is obtained. Furthermore, by setting the drying point until the point of releasing the holding of both edges, the dispersion of stretching axis can be reduced. The drying point means a site where the surface temperature of film becomes equal to the atmosphere temperature in the environment. From the above-described reason, the drying speed is also preferably as high as possible.

<Volatile Content Ratio Reduction Rate>

The volatile content ratio reduction rate as used in the present invention means a decrease per unit time of the volatile component contained per the unit volume. If the volatile content ratio reduction rate is low, shrinking takes time and during it, the stretched and oriented polymer film is liable to undergo dispersion of orientation, as a result, dispersion is readily generated in the

polarizing performance, single plate transmittance and the like. Accordingly, the volatile content ratio reduction rate is preferably higher, specifically, the reduction rate is preferably 1%/min or more.

5           Other requirements in the present invention are described below.

<Drying Temperature>

The polymer film must be dried until it is combined with a protective film and therefore, in the case of  
10   preparing a polarizing plate using a polyvinyl alcohol film, the drying temperature is preferably from 40 to 90°C, more preferably from 60 to 85°C.

<Swelling Percentage>

In the present invention, when the polymer film is  
15   polyvinyl alcohol and a hardening agent is used, the swelling percentage with water is preferably different between before and after the stretching so as not to relieve but to keep the state of being stretched in the oblique direction. More specifically, it is preferred that  
20   the swelling percentage before stretching is high and the swelling percentage after stretching and drying becomes low. More preferably, the swelling percentage with water before stretching is larger than 3% and the swelling percentage after drying is 3% or less.

## &lt;Prescription of Bending Part&gt;

The rail of regulating the trajectory of the holding means in the present invention is often demanded to have a large bending ratio. For the purpose of avoiding interference of film gripping means with each other due to abrupt bending or avoiding local concentration of stress, the trajectory of the gripping means preferably draws a circular arc at the bending part.

## &lt;Stretching Speed&gt;

In the present invention, the speed at which the film is stretched is preferably higher and when expressed by the stretching magnification per unit time, this is 1.1 times/min or more, preferably 2 times/min or more.

## &lt;Foreign Matters&gt;

In the present invention, if foreign matters are adhering to the polymer film before stretching, the surface becomes coarse. Therefore, the foreign matters are preferably removed. If foreign matters are present, particularly at the time of manufacturing a polarizing plate, these cause color/optical unevenness. It is also important that foreign matters do not adhere to the polymer film until a protective film is combined. Therefore, the polarizing plate is preferably manufactured in an environment where the floating dusts are reduced as much as possible. The amount of foreign matters as used in the

present is a value obtained by dividing the weight of foreign matters adhering to the film surface by the surface area and is expressed by the gram number per square meter. The amount of foreign matters is preferably 1 g/m<sup>2</sup> or less, 5 more preferably 0.5 g/m<sup>2</sup> or less. The smaller amount is more preferred.

The method for removing foreign matters is not particularly limited and any method may be used as long as it can remove the foreign matters without adversely 10 affecting the polymer film before stretching. Examples thereof include a method of jetting a water flow to scrape off the foreign matters, a method of scraping off the foreign matters by a gas jet, and a method of scraping off the foreign matters using a blade of cloth, rubber or the 15 like.

#### <Tension in Longitudinal Direction>

In the present invention, at the time of holding both edges of the film by holding means, the film is preferably tensioned to facilitate the holding. Specific examples of 20 the method therefor include a method of applying a tension in the longitudinal direction to make the film tense. The tension varies depending on the state of film before stretching but is preferably applied to such a degree of not loosening the film.

## &lt;Temperature at Stretching&gt;

In the present invention, the ambient temperature at the time of stretching the film may be sufficient if it is at least higher than the solidification point of volatile content contained in the film. In the case where the film is polyvinyl alcohol, the ambient temperature is preferably 25°C or more. In the case of stretching polyvinyl alcohol dipped in iodine/boric acid for the manufacture of a polarizing film, the ambient temperature is preferably from 30 to 90°C.

## &lt;Humidity at Stretching&gt;

In the case of stretching polyvinyl alcohol which is a film having water as the volatile content, the film is preferably stretched in a humidity conditioning atmosphere. Particularly, when a hardening agent is imparted, if the water content decreases, the hardening of film proceeds and the stretching becomes difficult. Therefore, the humidity is preferably 50% or more, more preferably 80% or more, still more preferably 90% or more.

## 20 &lt;Conveyance Speed in Longitudinal Direction&gt;

In the case of stretching a polyvinyl alcohol film imparted with a hardening agent, as the stretching time passes, the hardening of the film proceeds. Therefore, the travelling speed in the longitudinal direction is preferably 1 m/min or more. A higher speed is preferred in

view of productivity. In any case, the upper limit varies depending on the film stretched and the stretching machine.

<Polarizing Film>

In the present invention, the polymer film to be stretched is not particularly limited and a film comprising a polymer having appropriate thermoplasticity may be used. Examples of the polymer include PVA, polycarbonate, cellulose acylate and polysulfone.

The thickness of the film before stretching is not particularly limited, however, in view of stability of film holding and uniformity of stretching, the thickness is preferably from 1  $\mu\text{m}$  to 1 mm, more preferably from 20 to 200  $\mu\text{m}$ .

In the case of using the present invention for the production of a polarizing film, the polymer is preferably PVA. PVA is usually obtained by saponifying polyvinyl acetate but may contain a component copolymerizable with vinyl acetate, such as unsaturated carboxylic acid, unsaturated sulfonic acid, olefins and vinyl ethers. Also, a modified PVA containing an acetoacetyl group, a sulfonic acid group, a carboxyl group, an oxyalkylene group or the like may be used.

The saponification degree of PVA is not particularly limited but in view of solubility and the like, is preferably from 80 to 100 mol%, more preferably from 90 to

100 mol%. Also, the polymerization degree of PVA is not particularly limited but is preferably from 1,000 to 10,000, more preferably from 1,500 to 5,000.

<Dyeing Formulation/Method>

5           The polarizing film is obtained by dyeing a polymer film for polarizing film, such as PVA, and the dyeing step is performed by gas-phase or liquid-phase adsorption. As an example of the liquid-phase dyeing, when iodine is used as the polarizer, the dyeing is performed by dipping the  
10 polymer film for polarizing film in an aqueous iodine-potassium iodide solution. The iodine is preferably from 0.1 to 20 g/liter, potassium iodide is preferably from 1 to 200 g/liter and the weight ratio of iodine to potassium iodide is preferably from 1 to 200. The dyeing time is  
15 preferably from 10 to 5,000 seconds and the liquid temperature is preferably from 5 to 60°C. The dyeing method is not limited only to dipping but any means can be used, such as coating or spraying of iodine or a dye solution. The dyeing step may be provided either before or  
20 after the stretching step of the present invention, however, the dyeing is preferably performed in liquid phase before the stretching step because the film is appropriately swelled and the stretching thereof is facilitated.

<Polarizer>

25           In addition to iodine, it is also preferred to use a



dichromatic dye as the polarizer and dye the film with the dichromatic dye. Specific examples of the dichromatic dye include dye-type compounds such as azo-base dye, stilbene-base dye, pyrazolone-base dye, triphenyl methane-base dye, quinoline-base dye, oxazine-base dye, thiadine-base dye and anthraquinone-base dye. A water-soluble compound is preferred but the present invention is not limited thereto. Also, a hydrophilic substituent such as sulfonic acid group, amino group and hydroxyl group is preferably introduced into these dichromatic molecules. Specific examples of the dichromatic molecule include C.I. Direct Yellow 12, C.I. Direct Orange 39, C.I. Direct Orange 72, C.I. Direct Red 39, C.I. Direct Red 79, C.I. Direct Red 81, C.I. Direct Red 83, C.I. Direct Red 89, C.I. Direct Violet 48, C.I. Direct Blue 67, C.I. Direct Blue 90, C.I. Direct Green 59, C.I. Acid Red 37 and dyes described in JP-A-62-70802, JP-A-1-161202, JP-A-1-172906, JP-A-1-172907, JP-A-1-183602, JP-A-1-248105, JP-A-1-265205 and JP-A-7-261024. These dichromatic molecules are used as a free acid, an alkali metal salt, an ammonium salt or a salt of amines. By blending two or more of these dichromatic molecules, a polarizer having various colors can be produced. A polarizing device or polarizing plate where a compound (dye) of providing black color when polarization axes are orthogonally crossed is blended or various dichromatic molecules are blended to provide black

color is preferred because of its excellent single plate transmittance and polarization ratio.

The stretching method of the present invention is also preferably used in the production of a so-called  
5 polyvinylene-base polarizing film, where PVA is dehydrated or polyvinyl chloride is dechlorinated to form a polyene structure and the polarization is obtained by the conjugate double bond.

<Addition of Hardening Agent (Crosslinking Agent), Metal  
10 Salt>

The hardening agent (crosslinking agent) is described by referring to the case where a PVA film is used as the polymer film for the polarization film. In the process of producing a polarizing film by stretching a PVA film, a  
15 hardening agent capable of crosslinking the PVA film is preferably used. Particularly, when the oblique stretching method of the present invention is used, if the PVA film is not sufficiently hardened at the outlet of the stretching step, the orientation direction of the PVA film may be  
20 shifted due to tension in the step. Therefore, a hardening agent (crosslinking agent) is preferably incorporated into the PVA film by dipping the PVA film in a hardening agent (crosslinking agent) solution in the step before stretching or in the stretching step or by coating the solution. The  
25 means to impart the hardening agent (crosslinking agent) to

the PVA film is not particularly limited and any method such as dipping, coating or spraying the film in or with the solution may be used, however, a dipping method and a coating method are preferred. As the coating means, any  
5 commonly known means such as roll coater, die coater, bar coater, slide coater and curtain coater may be used. Also, a method of bringing a cloth, cotton, porous material or the like impregnated with the solution into contact with the film is preferred. As the hardening agent  
10 (crosslinking agent), those described U.S. Re232897 can be used, however, boric acid and borax are preferably used in practice.

The hardening agent (crosslinking agent) may be imparted before or after the film is engaged in the  
15 stretching machine. This may be performed in any step until the end of the step (b) in examples shown in Figs. 3 and 4, where the stretching in the cross direction is substantially finished. After the hardening agent (crosslinking agent) is added, a rinsing/water washing step  
20 may be provided. In the above, the hardening agent is described by referring to the case of using a PVA film as the polymer film for the polarizing film, however, those described here can be mostly applied also to the case of using other polymer film by making slight changes according  
25 to the kind of the polymer.

The present invention is characterized in that a metal salt is present in the polarizing film and thereby, a high single plate transmittance is obtained while maintaining the orientation degree of the polarizer. This is considered to result because metal ion forms a salt with polyiodide ion due to the presence of the metal salt and a high-order ion species is stabilized.

The metal for use in the present invention is preferably a metal element capable of forming a polyvalent ion. In particular, a metal element belonging to the transition element is preferred. Specific examples thereof include zinc, cobalt, zirconium, iron, nickel and manganese. Among these, zinc is preferred.

The addition of the zinc is no particularly limited but the addition may be performed before dying, after dying, before stretching, after stretching, after drying or the step of attaching a polarizing film and a protective film. The zinc may be added as a zinc ion in a dying solution or a hardening solution, or may be added as another aqueous solution including the zinc prepared.

The method for adding the zinc is no particularly limited if the zinc may be added, but the addition may be performed by any one of methods including a dipping method, coating method and spraying method before dying, after dying, before stretching, after stretching, after drying or

the step of attaching a polarizing film and a protective film.

In order to add the zinc, the method of dissolving a zinc salt in each of the aqueous solutions may be exemplified. In the present invention, in view of easily producing, the method of dissolving a zinc salt in the hardening solution and adding the zinc in parallel with dipping in the hardening solution is preferable.

As the zinc salt, zinc halogen including zinc chloride and zinc iodide, zinc sulfate, or zinc acetate may be exemplified. The used amount of the zinc salt may properly be selected if the content of the zinc in the polarizing plate or the polarizing film obtained become the zinc content defined in the present invention, e.g., when adding the zinc by dipping, the used amount of the zinc salt may be optionally determined, dependent on a zinc concentration in a dipping solution, dipping time and dipping temperature. When the dipping time is from 60 to 200 second, and the dipping temperature is from 30 to 40°C, the used amount of zinc chloride is from 0.5 to 15 parts by weight, per 100 parts by weight of water, preferably from 0.7 to 5 parts by weight.

The zinc content in the polarizing plate or the polarizing film obtained is from 0.04 to 0.5wt%. When the zinc content is less than 0.04 wt% or exceed 0.5 wt%, the

durability under high temperature and high humidity tend to deteriorate, and the polarizing degree and single plate transmittance tend to deteriorate. The zinc content in the polarizing plate or the polarizing film is a value shown a weight of the zinc in the polarizing plate of 100 weight parts by percentage.

The method for adding the metal salt to the film is no particularly limited but the addition may be performed in any one step of the step of dyeing the film with a polarizer, the step of adding a hardening agent to the film and the step of combining a polarizing film and a protective film. Among these, the metal ion is preferably added in the step of dyeing the film with a polarizer and/or the step of adding a hardening agent to the film.

In a more preferred embodiment, from 0.01 to 10.0 wt% of a metal salt is added to both an aqueous iodine/potassium iodide solution as the aqueous polarizer solution and an aqueous boric acid/potassium iodide solution as the aqueous hardening agent solution, whereby the dyeing of the film and the addition of a hardening agent to the film are performed and at the same time, the addition of the metal salt is performed. In a still more preferred embodiment, from 0.01 to 10.0 wt% of a metal salt is added only to an aqueous boric acid/potassium iodide solution as the aqueous hardening agent solution, whereby the addition of a

hardening agent and the addition of a metal salt are performed.

The shrinking of the stretched polymer film may be performed in either step during or after stretching. For  
5 shrinking the film, a method of heating the film and thereby removing the volatile content may be used, however, any means may be used if it can shrink the film. The volatile content after drying is preferably 3% or less, more preferably 2% or less, still more preferably 1.5% or  
10 less.

As such, in a preferred embodiment of the present invention, the stretching method comprises

- (i) stretching the film to 1.1 to 20.0 times at least in the cross direction,
- 15 (ii) giving a difference of 1% or more in the film travelling speed between both edges in the machine direction of the holding device,
- (iii) bending the film travelling direction while holding both edges of the film, such that the tilt angle  
20 between the film travelling direction at the outlet in the step of holding both edges of the film and the substantial stretching direction of the film becomes 20 to 70°,
- (iv) stretching the film while keeping the supporting property of the polymer film and allowing 5% or  
25 more of volatile content to be present, and then shrinking

the film to reduce the volatile content.

The rail of regulating the trajectory of the holding means is often demanded to have a large bending ratio. For the purpose of avoiding interference of film gripping means with each other due to abrupt bending or avoiding local concentration of stress, the trajectory of the gripping means preferably draws a circular arc at the bending part.

For attaching a protective film to the polarizing film thus produced by oblique stretching, for example, a method of attaching the protective film to the polarizing film using an adhesive while keeping the state of holding both edges in the above-described drying step of the polarizing film and then cutting both edges, or a method of removing the polarizing film from the both edges-holding part after drying, cutting both edges of the film and attaching a protective film thereto may be used.

Fig. 2 shows an example of punching the polarizing plate obtained by oblique stretching (an example of  $45^\circ$  inclination). As shown in Fig. 2, since the stretching axis 81, namely, absorption axis of polarization is inclined at  $45^\circ$  with respect to the longitudinal direction 82 and the absorption axis 71 of the protective film is in parallel to the longitudinal direction, the tilt angle therebetween becomes  $45^\circ$ . Moreover, the angle of the absorption axis 81 of polarization agrees with the angle



made, when attached with a liquid crystal cell in LCD, between the absorption axis of the polarizing plate and the vertical or transverse direction of the liquid crystal cell itself, therefore, oblique punching is not necessary in the punching step. Also, as seen from Fig. 2, since the obliquely stretched polarizing plate is cut in a straight line along the longitudinal direction, a practical polarizing plate can also be produced without punching the lengthy polarizing plate but by slitting it along the longitudinal direction, as a result, remarkably high productivity is attained.

From the standpoint of elevating the contrast of a liquid crystal display, the polarizing plate of the present invention preferably has a high transmittance and a high polarization degree. The transmittance is preferably 30% or more, more preferably 40% or more, at 550 nm. The polarization degree is preferably 95.0% or more, more preferably 99% or more, still more preferably 99.9% or more, at 550 nm. In the present invention, unless otherwise indicated, the transmittance means a single plate transmittance.

The polarizing plate of the present invention is preferably used for a liquid crystal display. The liquid crystal display generally comprises a liquid crystal display element and a polarizing plate. The liquid crystal

display element comprises a liquid crystal layer, a substrate for holding the liquid crystal layer, and an electrode layer applying a voltage to the liquid crystal. The substrate and the electrode layer each is produced  
5 using a transparent material for the purpose of display. As the transparent substrate, a glass thin plate or a resin film is used. In the case of a liquid crystal display required to have some flexuosity, a resin film must be used. In addition to high transparency, the liquid crystal  
10 substrate is required to have low birefringence and heat resistance. A phase difference plate is sometimes provided in the liquid crystal display. The phase difference plate is a birefringent film for removing coloration on the liquid crystal picture element and realizing black-and-  
15 white expression. The phase difference plate is also produced by using a resin film. The phase difference plate is required to have a high birefringence. The polarizing plate comprises a protective film and a polarizing film. The polarizing film is a resin film using iodine or a  
20 dichromatic dye as a polarization element. The protective film is provided on one surface or both surfaces of the polarizing film for the purpose of protecting the polarizing film. In the case of providing the protective film only one surface of the polarizing film, the above-  
25 described liquid crystal substrate generally serves as the

protective film on the other surface. The protective film of a polarizing plate is required to have transparency and low birefringence (low retardation value) and the cellulose acetate film of the present invention is particularly  
5 advantageously used therefor.

The polarizing film of a polarizing plate includes iodine-type polarizing film, a dye-type polarizing film using a dichromatic dye, and a polyene-type polarizing film. Any of these polarizing films is generally produced using a  
10 polyvinyl alcohol-type film. The protective film of a polarizing plate preferably has a thickness of 25 to 350  $\mu\text{m}$ , more preferably from 50 to 200  $\mu\text{m}$ . In the protective film, an ultraviolet absorbent, a slipping agent, a deterioration inhibitor and a plasticizer may be added. On the  
15 protective film of a polarizing plate, a surface-treating film may be further provided. The function of the surface-treating film includes hard coat, anticlouding treatment, antiglare treatment and antireflection treatment. The polarizing plate and the protective film thereof are  
20 described in JP-A-4-219703, JP-A-5-212828 and JP-A-6-51117. The protective film of a polarizing plate preferably has a thickness of 10 to 350  $\mu\text{m}$ , more preferably from 25 to 200  $\mu\text{m}$ .

On the protective film surface of the polarizing  
25 plate of the present invention, any functional layer can be

provided such as an optical anisotropic layer for compensating the view angle of LCD, an antiglare layer or antireflection layer for improving visibility of the display, or a layer (e.g., polymer dispersion liquid crystal layer, cholesteric liquid crystal layer) having a function of separating PS wave due to anisotropic scattering or anisotropic optical interference for improving the brightness of LCD described in JP-A-4-229828, JP-A-6-75115 and JP-A-8-50206, a hard coat layer for elevating scratch resistance of the polarizing plate, a gas barrier layer for preventing diffusion of water content or oxygen, an easily adhesive layer for elevating the adhesive strength to polarizing film, adhesive or pressure-sensitive adhesive, or a layer for imparting slipperiness.

The functional layer may be provided in the polarizing film side or on the surface opposite the polarizing film. The side where the functional layer is provided is appropriately selected according to the purpose.

On one surface or both surfaces of the polarizing film of the present invention, various functional films can be directly attached as a protective film. Examples of the functional film include a phase difference film such as  $\lambda/4$  plate and  $\lambda/2$  plate, a light diffusion film, a plastic cell having an electroconductive layer provided on the surface opposite the polarizing plate, a brightness improving film

having an anisotropic scattering or anisotropic optical interference function, a reflective plate, and a reflective plate having a transflective function.

As the protective film of the polarizing plate, one  
5 sheet of the above-described protective film or a plurality of sheets may be stacked. The same protective film may be attached to both surfaces of the polarizing film or protective films attached to both surfaces may have different functions and physical properties from each other.  
10 It is also possible to attach the above-described protective film only to one surface and not attach the protective film to the opposite surface but directly provide thereon a pressure-sensitive adhesive layer for directly attaching thereto a liquid crystal cell. In this  
15 case, a releasable separator film is preferably provided in the outer side of the pressure-sensitive adhesive.

#### <Combining Angle of Protective Film and Polarizing Film>

In the present invention, when the protective film and the polarizing film are combined at an angle to run the  
20 orientation axis (phase lag axis) of the protective film and the stretching axis (absorption axis) of the polarizing film not in parallel, an effect of giving excellent dimensional stability is provided. For obtaining this effect, the angle is preferably from no less than 10° to  
25 less than 90°, more preferably from 20° to less than 70°.

<Protective Film>

A protective film is attached to both surfaces or one surface of the polarizing film produced in the present invention and the laminate is used as a polarizing plate.

5 The kind of the protective film is not particularly limited and, for example, cellulose acylates such as cellulose acetate and cellulose acetate butyrate, polycarbonate, polyolefin, polystyrene and polyester can be used. The protective film of a polarizing plate is required to have  
10 properties such as transparency, appropriate moisture permeability, low birefringence and appropriate rigidity and from overall view, cellulose acylates are preferred and cellulose acetate is more preferred.

The protective film may have any physical property  
15 values according to use end and representative preferred values in the case of using the protective film for normal transmission-type LCD are described below. In view of handleability and durability, the film thickness is preferably from 5 to 500  $\mu\text{m}$ , more preferably from 20 to  
20 200  $\mu\text{m}$ , still more preferably from 20 to 100  $\mu\text{m}$ . The retardation value is preferably from 0 to 150 nm, more preferably from 0 to 20 nm, still more preferably from 0 to 10 nm, particularly preferably from 0 to 5 nm, at 632.8 nm. The phase lag axis of the protective film preferably runs  
25 substantially in parallel or orthogonally to the absorption

axis of the polarizing film from the standpoint of avoiding the elliptic formation of the linear polarization. However, this does not apply when the protective film is imparted with a function of changing the polarization property, such as phase difference plate, and the absorption axis of the polarizing plate can make any angle with the phase lag axis of the protective film.

The visible light transmittance is preferably 60% or more, more preferably 90% or more. The dimensional decrease after the treatment at 90°C for 120 hours is preferably from 0.3 to 0.01%, more preferably from 0.15 to 0.01%. The tensile strength in the film tensile test is preferably from 50 to 1,000 MPa, more preferably from 100 to 300 MPa. The moisture permeability of the film is preferably from 100 to 800 g/m<sup>2</sup>·day, more preferably from 300 to 600 g/m<sup>2</sup>·day.

Of course, the present invention is not limited these values.

The cellulose acylate which is preferred as the protective film is described in detail below. In a preferred cellulose acylate, the substitution degree to the hydroxyl group of cellulose satisfies all of the following formulae (I) to (IV):

$$(I) \quad 2.6 \leq A+B \leq 3.0$$

(II)  $2.0 \leq A \leq 3.0$

(III)  $0 \leq B \leq 0.8$

(IV)  $1.9 < A - B$

wherein A and B each represents a substitution degree of an acyl group substituted to the hydroxyl group of cellulose, A is a substitution degree of an acetyl group and B is a substitution degree of an acyl group having from 3 to 5 carbon atoms. Cellulose has three hydroxyl groups in one glucose unit and the numerals above show the substitution degree for the hydroxyl group 3.0 and the maximum substitution degree is 3.0. In cellulose triacetate, the substitution degree A is generally from 2.6 to 3.0 (in this case, the hydroxyl group not substituted is maximally 0.4) and B is 0. The cellulose acylate used as a protective film of a polarizing plate is preferably cellulose triacetate where the acyl groups all are acetyl group, or cellulose acylate where the acetyl group is 2.0 or more, the acyl group having from 3 to 5 carbon atoms is 0.8 or less and the hydroxyl group not substituted is 0.4 or less. The acyl group having from 3 to 5 carbon atoms is more preferably 0.3 or less in view of physical properties. The substitution degree can be obtained by calculating from the measured bonding degrees of acetic acid and fatty acid having from 3 to 5 carbon atoms substituted to the hydroxyl group of cellulose. The measurement may be performed by



the method according to ASTM D-817-91.

The acyl group having from 3 to 5 carbon atoms other than acetyl group includes a propionyl group ( $\text{C}_2\text{H}_5\text{CO}-$ ), a butyryl group ( $\text{C}_3\text{H}_7\text{CO}-$ ) (n-, iso-) and a valeryl group  
5 ( $\text{C}_4\text{H}_9\text{CO}-$ ) (n-, iso-, sec-, tert-). Among these, n-substituted groups are preferred in view of mechanical strength of film formed, easy dissolution and the like, and an n-propionyl group is more preferred. If the substitution degree of acetyl group is low, the mechanical  
10 strength and resistance against humidity and heat decrease. When the substitution degree of acyl group having from 3 to 5 carbon atoms is high, the dissolution property in an organic solvent is enhanced but when respective substitution degrees are within the above-described ranges,  
15 good physical properties are attained.

The polymerization degree (viscosity average) of cellulose acylate is preferably from 200 to 700, more preferably from 250 to 550. The viscosity average degree of polymerization can be measured by the Ostwald viscometer.  
20 From the intrinsic viscosity  $[\eta]$  of cellulose acylate measured, the polymerization degree can be determined according to the following formula:

$$\text{DP} = [\eta] / K_m$$

(wherein DP is a viscosity average degree of polymerization  
25 and  $K_m$  is a constant of  $6 \times 10^{-4}$ ).

The cellulose as a raw material of the cellulose acylate includes cotton linter and wood pulp but cellulose acylate obtained from any raw material cellulose can be used or a mixture thereof may also be used.

5       The cellulose acylate is usually produced by a solvent casting method. In the solvent casting method, a cellulose acylate and various additives are dissolved in a solvent to prepare a thick solution (hereinafter referred to as a "dope") and cast on an endless support such as drum  
10 or band and the solvent is vaporized to form a film. The dope is preferably prepared to have a solid content concentration of 10 to 40 wt%. The drum or band is preferably finished to have a mirror surface. The casting and drying method in the solvent casting method are  
15 described in U.S. Patents 2,336,310, 2,367,603, 2,492,078, 2,492,977, 2,492,978, 2,607,704, 2,739,069 and 2,739,070, British Patents 640,731 and 736,892, JP-B-45-4554, JP-B-49-5614, JP-A-60-176834, JP-A-60-203430 and JP-A-62-115035.

A method of casting two or more layers of dope is  
20 also preferably used. In the case of casting a plurality of dopes, the film may be produced by casting solutions containing the dope respectively from a plurality of casting ports provided at intervals in the running direction of the support to stack one on another and the  
25 methods described, for example, in JP-A-61-158414, JP-A-1-

122419 and JP-A-11-198285 can be applied. The film may be also formed by casing cellulose acylate solutions from two casting ports and this can be practiced by the methods described, for example, in JP-B-60-27562, JP-A-61-94724, 5 JP-A-61-947245, JP-A-61-104813, JP-A-61-158413 and JP-A-6-134933. Furthermore, the casting method described in JP-A-56-162617 may also be preferably used, where the flow of a high-viscosity dope is wrapped with a low-viscosity dope and the high-viscosity and low-viscosity dopes are 10 simultaneously extruded.

Examples of the organic solvent in which the cellulose acylate is dissolved include hydrocarbons (e.g., benzene, toluene), halogenohydrocarbons (e.g., methylene chloride, chlorobenzene), alcohols (e.g., methanol, ethanol, 15 diethylene glycol), ketones (e.g., acetone), esters (e.g., ethyl acetate, propyl acetate) and ethers (e.g., tetrahydrofuran, methyl cellosolve). Among these, halogenohydrocarbons having from 1 to 7 carbon atoms are preferred and methylene chloride is most preferred. In 20 view of solubility of cellulose acylate, strippability from support and physical properties of film such as mechanical strength and optical property, one or a plurality of alcohol(s) having from 1 to 5 carbon atoms is(are) preferably mixed in addition to methylene chloride. The 25 content of alcohol is preferably from 2 to 25 wt%, more

preferably from 5 to 20 wt%, based on the solvent as a whole. Specific examples of the alcohol include methanol, ethanol, n-propanol, isopropanol and n-butanol. Among these, methanol, ethanol, n-butanol and a mixture thereof  
5 are preferred.

In addition to the cellulose acylate, the dope may arbitrarily contain, as the component which becomes a solid content after drying, a plasticizer, an ultraviolet absorbent, an inorganic fine particle, a heat stabilizer  
10 such as alkaline earth metal salt (e.g., calcium, magnesium), an antistatic agent, a flame retardant, a lubricant, an oil agent, a release accelerator from support, a hydrolysis inhibitor for cellulose acylate, and the like.

The plasticizer which is preferably added is a  
15 phosphoric acid ester or a carboxylic acid ester. Examples the phosphoric acid ester include triphenyl phosphate (TPP), tricresyl phosphate (TCP), cresyl diphenyl phosphate, octyl diphenyl phosphate, diphenyl biphenyl phosphate, trioctyl phosphate and tributyl phosphate. Representative examples  
20 of the carboxylic acid ester include phthalic acid ester and citric acid ester. Examples of the phthalic acid ester include dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), diphenyl phthalate (DPP) and diethylhexyl phthalate (DEHP).  
25 Examples of the citric acid ester include triethyl O-

acetylcitrate (OACTE), tributyl O-acetylcitrate (OACTB), acetyl triethyl citrate and acetyl tributyl citrate.

Examples of other carboxylic acid esters include butyl oleate, methylacetyl ricinoleate, dibutyl sebacate  
5 and trimellitic acid esters such as trimethyl trimellitate. Examples of the glycolic acid ester include triacetin, tributyrin, butylphthalyl butyl glycolate, ethylphthalyl ethyl glycolate and methylphthalyl ethyl glycolate.

Among these plasticizers, preferred are triphenyl  
10 phosphate, biphenyl diphenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, tributyl phosphate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, diethylhexyl phthalate, triacetin, ethylphthalyl ethyl glycolate and trimethyl trimellitate, more preferred  
15 are triphenyl phosphate, biphenyl diphenyl phosphate, diethyl phthalate, ethylphthalyl ethyl glycolate and trimethyl trimellitate. These plasticizers may be used individually or in combination of two or more thereof. The amount of the plasticizer added is preferably from 5 to  
20 30 wt%, more preferably from 8 to 16 wt%, based on the cellulose acylate. These compounds may be added together with the cellulose acylate or solvent at the preparation of the cellulose acylate solution or may be added during or after the preparation of solution.

25 The ultraviolet absorbent may be freely selected

according to the purpose and, for example, salicylic acid ester-base, benzophenone-base, benzotriazole-base, benzoate-base, cyanoacrylate-base and nickel complex salt-base absorbents can be used. Among these, benzophenone-base, benzotriazole-base and salicylic acid ester-base absorbents are preferred. Examples of the benzophenone-base ultraviolet absorbent include 2,4-dihydroxybenzophenone, 2-hydroxy-4-acetoxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone and 2-hydroxy-4-(2-hydroxy-3-methacryloxy)propoxybenzophenone. Examples of the benzotriazole-base ultraviolet absorbent include 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-tert-butylphenyl)-benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-amylphenyl)-benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-butylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-5'-tert-octylphenyl)benzotriazole. Examples of the salicylic acid ester-base ultraviolet absorbent include phenyl salicylate, p-octylphenyl salicylate and p-tert-butylphenyl salicylate. Among these ultraviolet absorbents, preferred are 2-hydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-methoxybenzophenone, 2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-5'-tert-

butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-tert-  
amylphenyl)benzotriazole and 2-(2'-hydroxy-3',5'-di-tert-  
butylphenyl)-5-chlorobenzotriazole.

A plurality of absorbents different in the absorption  
5 wavelength are preferably used in combination because a  
high shielding effect can be obtained over a wide  
wavelength range. The amount of the ultraviolet absorbent  
is preferably from 0.01 to 5 wt%, more preferably from 0.1  
to 3 wt%, based on the cellulose acylate. The ultraviolet  
10 absorbent may be added simultaneously with the dissolution  
of cellulose acylate or may be added to the dope after the  
dissolution. In particular, a form of adding an  
ultraviolet absorbent solution to the dope using a static  
mixer or the like immediately before casting is preferred.

15 Examples of the inorganic fine particle added to the  
cellulose acylate include silica, kaolin, talc,  
diatomaceous earth, quartz, calcium carbonate, barium  
sulfate, titanium oxide and alumina, and these may be  
freely used according to the purpose. The fine particles  
20 are preferably dispersed in a binder solution by arbitrary  
means such as high-speed mixer, ball mill, attritor or  
ultrasonic disperser before adding these to the dope. The  
binder is preferably a cellulose acylate. It is also  
preferred to disperse the fine particle together with other  
25 additives such as ultraviolet absorbent. Any dispersion

solvent may be used but a dispersion solvent having a composition close to the dope solvent is preferred. The number average particle size of the particles dispersed is preferably from 0.01 to 100  $\mu\text{m}$ , more preferably from 0.1 to 10  $\mu\text{m}$ . The dispersion solution may be added simultaneously in the step of dissolving the cellulose acylate or may be added to the dope in any step, however, a form of adding the dispersion solution immediately before casting using a static mixer or the like is preferred, similarly to the ultraviolet absorbent.

As the release accelerator from support, a surfactant is effective and the surfactant is not particularly limited but examples thereof include phosphoric acid-base, sulfonic acid-base, carboxylic acid-base, nonionic and cationic surfactants. These are described, for example, in JP-A-61-243837.

In the case of using the cellulose acylate film for the protective film, hydrophilicity is preferably imparted to the film surface by means of saponification, corona treatment, flame treatment, glow discharge treatment or the like so as to enhance the adhesive property to PVA-type resin. It may be also possible to disperse a hydrophilic resin in a solvent having affinity for cellulose acylate and coat the solution to form a thin layer. Among these means, a saponification treatment is preferred because



planeness and physical properties of the film are not impaired. The saponification treatment is performed by dipping the film in an aqueous solution of an alkali such as caustic soda. After the treatment, the film is  
5 preferably neutralized with an acid in a low concentration and thoroughly washed with water so as to remove the excess alkali.

The alkali saponification treatment which is preferably used as the surface treatment of the cellulose  
10 acylate film is specifically described below. This treatment is preferably performed by a cycle of dipping the cellulose acylate film surface in an alkali solution, neutralizing it with an acidic solution, and water washing and then drying the film. Examples of the alkali solution  
15 include a potassium hydroxide solution and a sodium hydroxide solution. The normal concentration of hydroxide ion is preferably from 0.1 to 3.0N, more preferably from 0.5 to 2.0N. The alkali solution temperature is preferably from room temperature to 90°C, more preferably from 40 to  
20 70°C. The film is generally then washed with water and after passing an acidic aqueous solution, again washed with water to obtain a surface-treated cellulose acylate film. Examples of the acid used here include hydrochloric acid, nitric acid, sulfuric acid, acetic acid, formic acid,  
25 chloroacetic acid and oxalic acid. The concentration of

the acid is preferably from 0.01 to 3.0N, more preferably from 0.05 to 2.0N. In the case of using the cellulose acylate film as a transparent protective film of a polarizing plate, an acid treatment and an alkali treatment, 5 namely, saponification treatment for the cellulose acylate, are preferably performed in view of the adhesion to the polarizing film.

The surface energy of a solid obtained by such a method can be determined, as described in Nure no Kiso to 10 Oyo (Basis and Application of Wetting), Realize Sha (December 10, 1989), by a contact angle method, a wetting heat method or an adsorption method. Among these, the contact angle method is preferred and the contact angle of water is preferably from 5 to 90°, more preferably from 5 15 to 70°.

On the protective film surface of the polarizing plate of the present invention, any functional layer can be provided such as an optical anisotropic layer for compensating the view angle of LCD, an antiglare layer or 20 antireflection layer for improving visibility of the display, or a layer (e.g., polymer dispersion liquid crystal layer, cholesteric liquid crystal layer) having a function of separating PS wave due to anisotropic scattering or anisotropic optical interference for 25 improving the brightness of LCD described in JP-A-4-229828,

JP-A-6-75115 and JP-A-8-50206, a hard coat layer for elevating scratch resistance of the polarizing plate, a gas barrier layer for preventing diffusion of water content or oxygen, an easily adhesive layer for elevating the adhesive strength to polarizing film, adhesive or pressure-sensitive adhesive, or a layer for imparting slipperiness.

The functional layer may be provided in the polarizing film side or on the surface opposite the polarizing film. The side where the functional layer is provided is appropriately selected according to the purpose.

On one surface or both surfaces of the polarizing film of the present invention, various functional films can be directly attached as a protective film. Examples of the functional film include a phase difference film such as  $\lambda/4$  plate and  $\lambda/2$  plate, a light diffusion film, a plastic cell having an electroconductive layer provided on the surface opposite the polarizing plate, a brightness improving film having an anisotropic scattering or anisotropic optical interference function, a reflective plate, and a reflective plate having a transflective function.

As the protective film of the polarizing plate, one sheet of the above-described protective film or a plurality of sheets may be stacked. The same protective film may be attached to both surfaces of the polarizing film or protective films attached to both surfaces may have

different functions and physical properties from each other. It is also possible to attach the above-described protective film only to one surface and not attach the protective film to the opposite surface but directly  
5 provide thereon a pressure-sensitive adhesive layer for directly attaching thereto a liquid crystal cell. In this case, a releasable separator film is preferably provided in the outer side of the pressure-sensitive adhesive.

The protective film is usually fed in a roll form and  
10 preferably attached continuously to a lengthy polarizing plate so that the longitudinal directions can agree. Here, the orientation axis (phase lag axis) of the protective film may run in any direction but in view of simplicity and easiness of operation, the orientation axis of the  
15 protective film is preferably in parallel to the longitudinal direction.

The angle between the phase lag axis (orientation axis) of the protective film and the absorption axis (stretching axis) of the polarizing film is also not  
20 particularly limited and may be appropriately set according to the purpose of the polarizing plate. The absorption axis of the lengthy polarizing plate of the present invention is not in parallel to the longitudinal direction and therefore, when the protective film having an  
25 orientation axis in parallel to the longitudinal direction

is continuously attached to the length polarizing plate of the present invention, a polarizing plate where the absorption axis of the polarizing film and the orientation axis of the protective film are not in parallel is obtained.

5 The polarizing plate where the polarizing film and the protective film are combined such that the absorption axis of the polarizing film and the orientation axis of the protective film run not in parallel is excellent in the dimensional stability. This performance is advantageously

10 exerted particularly when the polarizing plate is used for a liquid crystal display. The tilt angle between the phase lag axis of the protective film and the absorption axis of the polarizing film is from no less than  $10^\circ$  to less than  $90^\circ$ , preferably from  $20^\circ$  to  $80^\circ$ . With this tilt

15 angle, the dimensional stability effect is highly exerted

<Adhesive>

The adhesive for combining the polarizing film and the protective film is not particularly limited and examples thereof include PVA-base resin (including modified

20 PVA such as acetoacetyl group, sulfonic acid group, carboxylic group and oxyalkylene group) and an aqueous solution of boron compound. Among these, PVA resin is preferred. To the PVA resin, a boron compound, an aqueous potassium iodide solution or the like may be added. The

25 thickness of the adhesive layer after drying is preferably

from 0.01 to 10  $\mu\text{m}$ , more preferably from 0.05 to 5  $\mu\text{m}$ .

<Pressure-Sensitive Adhesive Layer>

In the polarizing plate of the present invention, a pressure-sensitive adhesive layer for the adhesion with other liquid crystal display member may be provided. On the surface of the pressure-sensitive adhesive layer, a release film is preferably provided. The pressure-sensitive adhesive layer is of course optically transparent and also exhibits appropriate viscoelasticity and pressure-sensitive adhesive property. The pressure-sensitive adhesive layer for use in the present invention may be provided, for example, by forming and curing a film using a polymer of an adhesive or pressure-sensitive adhesive, such as acryl-base copolymer, epoxy-base resin, polyurethane, silicone-base polymer, polyether, butyral-base resin, polyamide-base resin, polyvinyl alcohol-base resin or synthetic rubber, by a drying method, a chemical curing method, a heat curing method, a heat melting method or a photo-curing method. Among these, an acryl-base copolymer is most preferred because the pressure-sensitive adhesive properties can be easily controlled and the transparency, weather resistance and durability are excellent.

<Through Step>

In the present invention, a drying step of shrinking the stretched film to reduce the volatile content ratio and

after attaching the protective film at least to one surface of the film after or during drying, a step of after-heating the film are preferably provided. Specific examples of the method for attaching the protective film include a method of attaching the protective film to the polarizing film using an adhesive while keeping the state of holding both edges of the polarizing film during the drying step and then cutting both edges, and a method of releasing the polarizing film from the both edges-holding part after drying, cutting both edges of the film and attaching a protective film thereto. For cutting edges, a general technique may be used, for example, a method of cutting edges using a cutter such as edged tool or a method of using a laser. The combined films are preferably heated so as to dry the adhesive and improve the polarizing performance. The heating condition varies depending on the adhesive but in the case of an aqueous adhesive, the heating temperature is preferably 30°C or more, more preferably from 40 to 100°C, still more preferably from 50 to 80°C. These production steps are preferably performed in a through line in view of performance and production efficiency.

<Use, etc.>

The polarizing plate of the present invention can be used for various uses, however, by virtue of its

characteristic feature that the orientation axis is inclined with respect to the longitudinal direction, particularly the polarizing film where the tilt angle of the orientation axis is from 40 to 50° with respect to the longitudinal direction is preferably used as a polarizing plate for LCD (for example, in all liquid crystal modes such as TN, STN, OCB, ROCB, ECB, CPA, IPS and VA), a circularly polarizing plate for antireflection of organic EL displays, and the like.

Furthermore, the polarizing plate of the present invention is suitable also for uses combined with various optical members, for example, phase difference film such as  $\lambda/4$  plate and  $\lambda/2$  plate, view angle enlarged film, antiglare film and hard coat film.

The present invention is described in greater detail below by referring to Examples, however, the present invention is not limited thereto.

#### [Examples]

##### Example 1:

On one surface of a lengthy polyvinyl alcohol (PVA) film which was monoaxially stretched in the longitudinal direction (a polarizing film having an absorption axis in the longitudinal direction), a saponified film Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced



by Fuji Photo Film Co., Ltd. was attached using an aqueous 3% PVA (PVA-117H, produced by Kuraray Co., Ltd.) solution as the adhesive to provide 5 patterns (No. 1 to No. 5) of stretching axis as shown in Fig. 10.

5        Each of the obtained polarizing plates was evaluated as follows on the dimensional stability and warping due to aging in a dry constant humidity oven (D63) manufactured by Yamato Kagaku Sha. The results obtained are shown in Table 1.

10    {Dimensional Stability}

The shrinkage percentage after the treatment at 40°C and relative humidity of 30% for 100 hours was measured.

Dimensional shrinkage percentage:

- 15        ○: within 2%  
          △: 2-5%  
          ×: over 5%

{Warping}

20        The polarizing plate was heated in an atmosphere of 40°C and relative humidity of 30% for 100 hours and then left standing on a smooth surface. The presence or absence of warping was observed with an eye and evaluated by three stages.

Warping:

- 25        ○: Almost no warping.

△: Warped.

×: Heavily warped.

[Table 1]

No. of Polarizing Plate	Dimensional Stability	Warping	Remarks
No. 1	○	○	Invention
No. 2	○	○	Invention
No. 3	○	○	Invention
No. 4	×	×	Comparison
No. 5	×	×	Comparison

5

Example 2:

A PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 25°C for 90 seconds and further dipped  
10 in an aqueous solution containing 40 g/liter of boric acid and 30.0 g/liter of potassium iodide at 25°C for 120 seconds. Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 3 and after once stretched to 7.0 times in an atmosphere of 60°C and  
15 90%, shrunk to 5.3 times. Thereafter, while keeping constant the width, the film was dried at 70°C and removed from the tenter. The volatile content ratio of the PVA film was 31% before the initiation of stretching and 1.5% after the drying.

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center line of film delivered to the next step was 0°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling and slippage of film were not observed. The obtained polarizing film had a stretching axis inclined at 45° with respect to the longitudinal direction.

Thereafter, using an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution containing 4% of potassium iodide as the adhesive, saponified roll-form Fujitac (cellulose triacetate, retardation value: 3.0 nm, the stretching axis runs in parallel to the longitudinal direction) produced by Fuji Photo Film Co., Ltd. was continuously attached to the lengthy polarizing film while running the Fujitac in the longitudinal direction and dried at 80°C to obtain a polarizing plate having an effective width of 650 mm.

The polarizing plate was cut into a size of 310x233 mm as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to the side could be obtained. This polarizing plate had a transmittance of 43.3% and a polarization degree of 99.98% at 550 nm.

The measurement of retardation was performed at 632.8 nm using KOBRA21DH manufactured by Oji Test Instruments.

Example 3:

5 Iodine polarizing plates 91 and 92 prepared in Example 2 were used as two sheets of polarizing plates between which a liquid crystal cell 97 for LCD was interposed. As shown in Fig. 9, the polarizing plate 91 was disposed as a polarizing plate in the display side and  
10 attached to the liquid crystal cell 97 through an adhesive to prepare LCD.

The thus-prepared LCD exhibited excellent brightness, view angle property and visibility and even after allowing to stand for 100 hours in an atmosphere of 40°C and 30% RH,  
15 the polarizing plate was not separated from the liquid crystal display, revealing that the LCD was in a level of causing no trouble in the display properties.

[Example 4]

A PVA film was dipped in an aqueous solution  
20 containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 30°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at 30°C for 120 seconds. Subsequently, the film was introduced into a tenter  
25 stretching machine in the form of Fig. 3 and after once

stretched to 6.4 times in an atmosphere of 50°C and 95%,  
shrunk to 4.5 times. Thereafter, while keeping constant  
the width, the film was dried at 70°C and removed from the  
tenter. The edges of 3 cm in the cross direction were cut  
5 using a cutter and then the PVA film was attached with  
saponified Fujitac (cellulose triacetate, retardation  
value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using  
as the adhesive an aqueous solution containing an aqueous  
3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution  
10 and 4% of potassium iodide and further heated at 60°C for  
30 minutes to manufacture a polarizing plate having an  
effective width of 650 mm.

The water content of PVA film was 30% before the  
initiation of stretching and 1.5% after the drying. The  
15 water content reduction rate during shrinking was 5%/min  
and the drying point was present in the middle of the zone  
(c).

The difference in the conveyance speed between right  
and left tenter clips was less than 0.05% and the angle  
20 made by the center line of film introduced and the center  
line of film delivered to the next step was 0°. Here,  $|L1-L2|$   
was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$   
was established. At the outlet of the tenter, wrinkling  
and deformation of film were not observed.

25 The absorption axis direction of the obtained

polarizing plate was inclined at  $45^\circ$  with respect to the longitudinal direction. The inclination of the absorption axis of this polarizing plate was examined at intervals of 50 mm in the cross direction, as a result, the average tilt angle of the stretching axis with respect to the longitudinal direction was  $45^\circ$  and the dispersion thereof was  $\pm 0.5^\circ$ . The transmittance and polarization degree of this polarizing plate at 550 nm were examined at intervals of 50 mm in the plane per  $1 \text{ m}^2$ , as a result, the average transmittance was 40.2% and the average polarization degree was 99.56%.

Furthermore, the polarizing plate was cut into a size of  $310 \times 233 \text{ mm}$  as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at  $45^\circ$  with respect to the side could be obtained.

[Example 5]

A PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at  $40^\circ\text{C}$  for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at  $40^\circ\text{C}$  for 60 seconds. Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 4 and stretched to 4.5 times in an atmosphere of  $65^\circ\text{C}$  and 95%. Then, the

tenter was bent in the stretching direction as shown in Fig. 4 and thereafter, while keeping constant the width and undergoing shrinking, the film was dried in an atmosphere of 80°C and removed from the tenter. The edges of 3 cm in the cross direction were cut using a cutter and then the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution and 4% of potassium iodide and further heated at 60°C for 30 minutes to manufacture a polarizing plate having an effective width of 650 mm.

The water content of PVA film was 30.5% before the initiation of stretching and 1.5% after the drying. The water content reduction rate during shrinking was 10%/min and the drying point was present at the point of 1/3 of the zone (c).

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center line of film delivered to the next step was 46°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. The substantial stretching direction Ax-Cx at the tenter outlet was inclined at 45° with respect to the center line of film delivered to the

next step. At the outlet of the tenter, wrinkling and deformation of film were not observed.

5 The absorption axis direction of the obtained polarizing plate was inclined at  $45^\circ$  with respect to the longitudinal direction. The inclination of the absorption axis of this polarizing plate was examined at intervals of 50 mm in the cross direction, as a result, the average tilt angle of the stretching axis with respect to the longitudinal direction was  $45^\circ$  and the dispersion thereof  
10 was  $\pm 0.25^\circ$ . The transmittance and polarization degree of this polarizing plate at 550 nm were examined at intervals of 50 mm in the plane per  $1 \text{ m}^2$ , as a result, the average transmittance was 42.2% and the average polarization degree was 99.97%.

15 Furthermore, the polarizing plate was cut into a size of  $310 \times 233 \text{ mm}$  as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at  $45^\circ$  with respect to the side could be obtained.

20 [Comparative Example 2]

A PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at  $40^\circ\text{C}$  for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid  
25 and 30 g/liter of potassium iodide at  $40^\circ\text{C}$  for 60 seconds.



Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 4 and stretched to 4.5 times. Then, the tenter was bent in the stretching direction as shown in Fig. 4 and thereafter, while keeping constant the width and shrinking, the film was dried in an atmosphere of 40°C and removed from the tenter. The edges of 3 cm in the cross direction were cut using a cutter and then the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution and 4% of potassium iodide and further heated at 60°C for 30 minutes to manufacture a polarizing plate having an effective width of 650 mm. The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction. The inclination of the transmission axis of this polarizing plate was examined at intervals of 50 mm in the cross direction, as a result, the average tilt angle of the stretching axis with respect to the longitudinal direction was 45° and the dispersion thereof was  $\pm 3\%$ . The transmittance and polarization degree of this polarizing plate at 550 nm were examined at intervals of 50 mm in the plane per 1 m<sup>2</sup>, as a result, the average transmittance was 41.1% and the average

polarization degree was 99.78%.

[Example 6]

Iodine-type polarizing plates 91 and 92 prepared in Example 5 were used as two sheets of polarizing plates between which a liquid crystal cell 93 for LCD was interposed. As shown in Fig. 9, the polarizing plate 91 was disposed as a polarizing plate in the display side and attached to the liquid crystal cell 93 through an adhesive to prepare LCD.

10 The thus-prepared LCD exhibited excellent brightness, view angle property and visibility and even after use for one month at 40°C and 30% RH, the display grade was not deteriorated.

(Measurement of Transmittance and Polarization Degree at  
15 550 nm)

The transmittance was measured by Shimadzu Auto-recording Spectrometer UV2100. Furthermore, from the transmittance  $H_0$  (%) when the absorption axes of superposed two polarizing plates were agreed and the transmittance  $H_1$   
20 (%) when the absorption axes were orthogonalized, the polarization degree  $P$  (%) was determined by the following formula:

$$P = [(H_0 - H_1) / (H_0 + H_1)]^{1/2} \times 100$$

(Measurement of Retardation)

25 The measurement was performed at 632.8 nm using

KOBRA21DH manufactured by Oji Test Instruments.

[Example 7]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 2 liter/min and water on the surface was splashed out by air blowing to reduce the foreign matters adhering to the surface to 0.5% or less. This PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 30°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at 30°C for 120 seconds. Subsequently, air was blown on both surfaces of the film to remove excess water to provide a state such that the distribution of the water content in the film was 2% or less. In this state, the film was introduced into a tenter stretching machine in the form of Fig. 3 and after once stretched to 6.4 times in an atmosphere of 45°C and 95%, shrunk to 4.5 times. Thereafter, while keeping constant the width, the film was dried at 80°C and removed from the tenter. The edges of 3 cm in the cross direction were cut using a cutter and then the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution

and 4% of potassium iodide and further heated at 60°C for 30 minutes to manufacture a polarizing plate having an effective width of 650 mm.

The water content of PVA film was 30% before the  
5 initiation of stretching and 1.5% after the drying. The water content reduction rate during shrinking was 5%/min.

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center  
10 line of film delivered to the next step was 0°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling and deformation of film were not observed.

The absorption axis direction of the obtained  
15 polarizing plate was inclined at 45° with respect to the longitudinal direction and also inclined at 45° with respect to the phase lag axis of Fujitac as the protective film.

The transmittance and polarization degree of this  
20 polarizing plate at 550 nm were examined at intervals of 50 mm in the plane per 1 m<sup>2</sup>, as a result, the average transmittance was 40.8%, the average polarization degree was 99.55%, and the dispersion of the maximum value and the minimum value was  $\pm 0.5\%$  in both the transmittance and the  
25 polarization degree.

Furthermore, the polarizing plate was cut into a size of 310×233 mm as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to the side could be  
5 obtained.

[Example 8]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 2 liter/min and water on the surface was splashed out by air blowing to  
10 reduce the foreign matters adhering to the surface to 0.5% or less. This PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid  
15 and 30 g/liter of potassium iodide at 40°C for 60 seconds. Subsequently, air was blown on both surfaces of the film to remove excess water to provide a state such that the distribution of the water content in the film was 2% or less. In this state, the film was introduced into a tenter  
20 stretching machine in the form of Fig. 4 and stretched to 4.5 times in an atmosphere of 65°C and 95%. The tenter was bent in the stretching direction as shown in Fig. 4 and thereafter, while keeping constant the width and undergoing shrinking, the film was dried in an atmosphere of 80°C and  
25 removed from the tenter. The edges of 3 cm in the cross

direction were cut using a cutter and then the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing  
5 an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution and 4% of potassium iodide and further heated at 60°C for 30 minutes to manufacture a polarizing plate having an effective width of 650 mm.

The water content of PVA film was 32% before the  
10 initiation of stretching and 1.5% after the drying. The water content reduction rate during shrinking was 10%/min.

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center  
15 line of film delivered to the next step was 46°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. The substantial stretching direction Ax-Cx at the tenter outlet was inclined at 45° with respect to the center line 22 of film delivered to the  
20 next step. At the outlet of the tenter, wrinkling and deformation of film were not observed.

The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction. The transmittance and polarization  
25 degree of this polarizing plate at 550 nm were examined at

intervals of 50 mm in the plane per 1 m<sup>2</sup>, as a result, the average transmittance was 42.9%, the average polarization degree was 99.97% and the dispersion of the maximum value and the minimum value was  $\pm 0.25\%$  in both the transmittance  
5 and the polarization degree.

Furthermore, the polarizing plate was cut into a size of 310×233 mm as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to the side could be  
10 obtained.

[Comparative Example 3]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 0.1 liter/min and water on the surface was splashed out by air blowing to  
15 reduce the foreign matters adhering to the surface to 2% or less. This PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid  
20 and 30 g/liter of potassium iodide at 40°C for 60 seconds. Subsequently, without air-blowing both surfaces of the film, the film in the state such that the distribution of water content in the film was 10% was introduced into a tenter stretching machine in the form of Fig. 4 and stretched to  
25 4.5 times. The tenter was bent in the stretching direction

as shown in Fig. 4 and thereafter, while keeping constant the width and undergoing shrinking, the film was dried in an atmosphere of 40°C and removed from the tenter. The edges of 3 cm in the cross direction were cut using a cutter and then the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution and 4% of potassium iodide and further heated at 60°C for 30 minutes to manufacture a polarizing plate having an effective width of 650 mm. Dyeing unevenness was generated over the entire surface of the film. The transmittance and polarization degree of this polarizing plate at 550 nm were examined at intervals of 50 mm in the plane per 1 m<sup>2</sup>, as a result, the average transmittance was 40.1%, the average polarization degree was 99.46% and the dispersion of the maximum value and the minimum value was ±3% in both the transmittance and the polarization degree.

[Example 9]

Iodine-type polarizing plates 91 and 92 prepared in Example 8 were used as two sheets of polarizing plates between which a liquid crystal cell 93 for LCD was interposed. As shown in Fig. 9, the polarizing plate 91 was disposed as a polarizing plate in the display side and



attached to the liquid crystal cell 93 through an adhesive to prepare LCD.

The thus-prepared LCD exhibited excellent brightness, view angle property and visibility and even after use for one month at 40°C and 30% RH, the display grade was not deteriorated.

(Measurement of Transmittance and Polarization Degree at 550 nm)

The transmittance was measured by Shimadzu Auto-recording Spectrometer UV2100. Furthermore, from the transmittance H0 (%) when the absorption axes of superposed two polarizing plates were agreed and the transmittance H1 (%) when the absorption axes were orthogonalized, the polarization degree P (%) was determined by the following formula:

$$P = [(H0 - H1) / (H0 + H1)]^{1/2} \times 100$$

(Measurement of Retardation)

The measurement was performed at 632.8 nm using KOBRA21DH manufactured by Oji Test Instruments.

[Example 10]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 2 liter/min and water on the surface was splashed out by air blowing to reduce the foreign matters adhering to the surface to 0.5% or less. This PVA film was dipped in an aqueous solution

containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 25°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at 25°C for 120 seconds.

5 Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 3 and after once stretched to 7.0 times in an atmosphere of 40°C and 95%, shrunk to 5.3 times. Thereafter, while keeping constant the width, the film was dried at 60°C and removed from the

10 tenter. The water content of PVA film was 30% before the initiation of stretching and 1.5% after the drying. The elastic modulus of PVA film before stretching was 35 MPa in an atmosphere of 40°C and 95%.

The difference in the conveyance speed between right

15 and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center line of film delivered to the next step was 0°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling

20 and deformation of film were not observed.

At this time, the surface roughness Ra of the polarizing plate was measured by a surface roughness tester (manufactured by Kosaka Laboratory Ltd.) and found to be 1.0  $\mu\text{m}$ .

25 Then, the PVA film was attached with saponified

Fujitac (cellulose triacetate, retardation value: 3.0 nm; the saponification of the cellulose acetate film was performed as follows: the cellulose acetate film was dipped in an aqueous 1.5N sodium hydroxide solution at 55°C for 2 minutes, washed in a water washing bath at room temperature, neutralized with 0.1N sulfuric acid at 30°C, again washed in the water washing bath at room temperature and then dried with hot air at 100°C) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing 3% of PVA (PVA-117H produced by Kuraray Co., Ltd.) and 4% of potassium iodide and further heated at 60°C for 30 minutes to obtain a polarizing plate having an effective width of 650 mm. By virtue of smooth surface, the films were attached with each other in a good state.

The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction and also inclined at 45° with respect to the phase lag axis of Fujitac (protective film). The transmittance of this polarizing plate at 550 nm was 41.3% and the polarization degree was 99.60%.

Furthermore, the polarizing plate was cut into a size of 310×233 mm as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to the side could be obtained. No color slippage streak was observed with an

eye.

[Example 11]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 2 liter/min and  
5 water on the surface was splashed out by air blowing to reduce the foreign matters adhering to the surface to 0.5% or less. This PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped  
10 in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at 40°C for 60 seconds. Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 4 and stretched to 4.5 times. The tenter was bent in the stretching direction  
15 as shown in Fig. 4 and thereafter, while keeping constant the width and undergoing shrinking, the film was dried in an atmosphere of 80°C and removed from the tenter. The edges of 3 cm in the cross direction were cut using a cutter and then the PVA film was attached with saponified  
20 Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using as the adhesive an aqueous solution containing 3% of PVA (PVA-117H produced by Kuraray Co., Ltd.) and 4% of potassium iodide and further heated at 60°C for 30 minutes to obtain a  
25 polarizing plate having an effective width of 650 mm.

The water content of PVA film was 32% before the initiation of stretching and 1.5% after the drying. The elastic modulus of PVA film before stretching was 25 MPa in an atmosphere of 40°C and 95%. The surface roughness Ra of the polarizing plate after drying was measured by the  
5 tester used in Example 10 and found to be 0.05  $\mu\text{m}$ .

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center  
10 line of film delivered to the next step was 46°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. The substantial stretching direction Ax-Cx at the tenter outlet was inclined at 45° with respect to the center line 22 of film delivered to the  
15 next step. At the outlet of the tenter, wrinkling and deformation of film were not observed.

The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction. The transmittance of this  
20 polarizing plate at 550 nm was 42.3% and the polarization degree was 99.97%. Furthermore, the polarizing plate was cut into a size of 310×233 mm as in Fig. 8, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to  
25 the side could be obtained. No color slippage streak was

observed with an eye.

[Comparative Example 4]

Both surfaces of a PVA film were washed with ion exchange water at a water flow rate of 2 liter/min and water on the surface was splashed out by air blowing to reduce the foreign matters adhering to the surface to 0.5% or less. This PVA film was dipped in an aqueous solution containing 1.0 g/liter of iodine and 120.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30 g/liter of potassium iodide at 40°C for 60 seconds. Subsequently, the film was dried at 60°C for 10 minutes. The water content of this PVA film was 1% and in this state, the elastic modulus was 800 MPa. Then, the PVA film was introduced into a tenter stretching machine in the form of Fig. 4 and stretched to 4.5 times. The tenter was bent in the stretching direction as shown in Fig. 4 and thereafter, while keeping constant the width and undergoing shrinking, the film was dried in an atmosphere of 80°C and removed from the tenter. Wrinkling remained over the entire surface of the film and the surface roughness Ra was 2 cm. Due to coarse roughness, a protective film could not be attached, failing in obtaining a polarizing plate. A large number of color slippage streaks were present throughout the surface.

## [Example 12]

Iodine-type polarizing plates 91 and 92 prepared in Example 11 were used as two sheets of polarizing plates between which a liquid crystal cell 97 for LCD was  
5 interposed. As shown in Fig. 9, the polarizing plate 91 was disposed as a polarizing plate in the display side and attached to the liquid crystal cell 97 through an adhesive to prepare LCD.

The thus-prepared LCD exhibited excellent brightness,  
10 view angle property and visibility and even after use for one month at 40°C and 30% RH, the display grade was not deteriorated.

(Measurement of Transmittance and Polarization Degree at 550 nm)

15 The transmittance was measured by Shimadzu Auto-recording Spectrometer UV2100. Furthermore, from the transmittance H0 (%) when the absorption axes of superposed two polarizing plates were agreed and the transmittance H1 (%) when the absorption axes were orthogonalized, the  
20 polarization degree P (%) was determined by the following formula:

$$P = [(H0 - H1) / (H0 + H1)]^{1/2} \times 100$$

(Measurement of Retardation)

25 The measurement was performed at 632.8 nm using

KOBRA21DH manufactured by Oji Test Instruments.

[Example 13]

<Preparation of Polarizing Plate>

A PVA film having a number average polymerization  
5 degree of 1,700 was dipped in an aqueous solution  
containing 1.0 g/liter of iodine and 60.0 g/liter of  
potassium iodide at 40°C for 90 seconds and further dipped  
in an aqueous solution containing 40 g/liter of boric acid  
and 30.0 g/liter of potassium iodide, where iron chloride  
10 was added to a concentration of 1.0 wt%, at 40°C for 120  
seconds. Subsequently, the film was introduced into a  
tenter stretching machine in the form of Fig. 3 and after  
once stretched to 7.0 times, shrunk to 5.3 times.  
Thereafter, while keeping constant the width, the film was  
15 dried at 60°C and removed from the tenter. The water  
content (volatile content ratio) of PVA film was 31% before  
the initiation of stretching and 1.5% after the drying.

The difference in the conveyance speed between right  
and left tenter clips was less than 0.05% and the angle  
20 made by the center line of film introduced and the center  
line of film delivered to the next step was 0°. Here,  $|L1-L2|$   
was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$   
was established. The substantial stretching direction Ax-  
Cx at the tenter outlet was inclined at 45° with respect to  
25 the center line 22 of film delivered to the next step. At



the outlet of the tenter, wrinkling and deformation of film were not observed.

Then, the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution as the adhesive and further dried at 80°C to obtain a polarizing plate having an effective width of 650 mm.

The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction and also inclined at 45° with respect to the phase lag axis of Fujitac.

The transmittance of this polarizing plate at 550 nm was 42.9% and the polarization degree was 99.89%.

Furthermore, the polarizing plate was cut into a size of 310×233 mm as in Fig. 2, as a result, a polarizing plate having an area efficiency of 91.5% and having an absorption axis inclined at 45° with respect to the side could be obtained.

The polarizing plate obtained was subjected to tests of heat resistance and humidity and heat resistance, as a result, the fluctuation width of the single plate transmittance was 9.2% and the fluctuation width of the polarization degree was 8.3%.

## &lt;Evaluation of Humidity and Heat Resistance&gt;

(Exposure to High Humidity and High Temperature)

The polarizing plate was left standing under an atmosphere at a temperature of 60°C and a humidity of 90% for 500 hours in a constant temperature and constant humidity oven (G-42M, manufactured by Yamato Kagaku Sha) and used as a measurement sample.

(Fluctuation Width of Transmittance)

The transmittance at 550 nm was measured using Shimadzu Auto-recording Spectrometer UV2100 and the fluctuation width was calculated according to the following formula:

Fluctuation width of transmittance (%) =

$$|T_1 - T_0| / T_0 \times 100$$

wherein  $T_1$  is a transmittance of a sample exposed to high humidity and high temperature and  $T_0$  is a transmittance before the exposure.

(Fluctuation Width of Polarization Degree)

The transmittance at 550 nm was measured using Shimadzu Auto-recording Spectrometer UV2100, the polarization degree  $P$  (%) was determined according to formula (1) and then, the fluctuation width was calculated according to the following formula:

Fluctuation width of polarization degree (%)

$$= |P_1 - P_0| / P_0 \times 100$$

wherein  $P_1$  is a polarization degree of a sample exposed to high humidity and high temperature and  $P_0$  is a polarization degree before the exposure.

<Evaluation of Heat Resistance>

5 (Exposure to High Temperature)

The polarizing plate was left standing under an atmosphere at a temperature of 80° and a humidity of 30% RH for 500 hours in Shimadzu Dry Constant Temperature Oven (D63) and used as a measurement sample.

10 (Evaluation of Fluctuation Width of Transmittance and Fluctuation Width of Polarization Degree)

The fluctuation width of the transmittance and the fluctuation width of the polarization degree were evaluated in the same manner as in <Evaluation of Humidity and Heat  
15 Resistance>.

[Example 14]

<Preparation of Polarizing Plate>

A PVA film having a number average polymerization degree of 1,700 was dipped in an aqueous solution  
20 containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30.0 g/liter of potassium iodide, where zinc chloride was added to a concentration of 1.0 wt%, at 40°C for 120  
25 seconds. Subsequently, the film was introduced into a

tenter stretching machine in the form of Fig. 3 and after once stretched to 7.0 times, shrunk to 5.3 times. Thereafter, while keeping constant the width, the film was dried at 60°C and removed from the tenter. The water content (volatile content ratio) of PVA film was 31% before the initiation of stretching and 1.5% after the drying.

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center line of film delivered to the next step was 0°. Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling and deformation of film were not observed.

Then, the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution as the adhesive and further dried at 80°C to obtain a polarizing plate having an effective width of 650 mm.

The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction and also inclined at 45° with respect to the phase lag axis of Fujitac.

The transmittance of this polarizing plate at 550 nm was 43.0% and the polarization degree was 99.95%.

The polarizing plate obtained was subjected to tests of heat resistance and humidity and heat resistance, as a result, the fluctuation width of the single plate transmittance was 2.4% and the fluctuation width of the polarization degree was 1.2%.

[Example 15]

<Preparation of Polarizing Plate>

A PVA film having a number average polymerization degree of 2,400 was dipped in an aqueous solution containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped in an aqueous solution containing 40 g/liter of boric acid and 30.0 g/liter of potassium iodide, where zinc chloride was added to a concentration of 1.0 wt%, at 40°C for 120 seconds. Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 3 and after once stretched to 7.0 times, shrunk to 5.3 times. Thereafter, while keeping constant the width, the film was dried at 60°C and removed from the tenter. The water content (volatile content ratio) of PVA film was 31% before the initiation of stretching and 1.5% after the drying.

The difference in the conveyance speed between right and left tenter clips was less than 0.05% and the angle made by the center line of film introduced and the center line of film delivered to the next step was 0°. Here, |L1-

L2| was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling and deformation of film were not observed.

Then, the PVA film was attached with saponified  
5 Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution as the adhesive and further dried at 80°C to obtain a polarizing plate having an effective width of 650 mm.

10 The absorption axis direction of the obtained polarizing plate was inclined at 45° with respect to the longitudinal direction and also inclined at 45° with respect to the phase lag axis of Fujitac.

The transmittance of this polarizing plate at 550 nm  
15 was 43.2% and the polarization degree was 99.74%.

The polarizing plate obtained was subjected to tests of heat resistance and humidity and heat resistance, as a result, the fluctuation width of the single plate transmittance was 0.8% and the fluctuation width of the  
20 polarization degree was 0.3%.

[Example 16]

#### <Preparation of Liquid Crystal Display>

Iodine-type polarizing films 91 and 92 prepared in Example 14 were used as two sheets of polarizing plates  
25 between which a liquid crystal cell 93 for LCD was

interposed. As shown in Fig. 9, the polarizing plate 91 was disposed as a polarizing plate in the display side and attached to the liquid crystal cell 93 through an adhesive to prepare LCD.

- 5           The thus-prepared LCD exhibited excellent brightness, view angle property and visibility and even after use for one month at 40°C and 30% RH, the display grade was not deteriorated.

[Comparative Example 5]

10   <Preparation of Polarizing Plate>

- A PVA film having a number average polymerization degree of 1,700 was dipped in an aqueous solution containing 1.0 g/liter of iodine and 60.0 g/liter of potassium iodide at 40°C for 90 seconds and further dipped  
15   in an aqueous solution containing 40 g/liter of boric acid and 30.0 g/liter of potassium iodide at 40°C for 120 seconds. Subsequently, the film was introduced into a tenter stretching machine in the form of Fig. 3 and after once stretched to 7.0 times, shrunk to 5.3 times.  
20   Thereafter, while keeping constant the width, the film was dried at 60°C and removed from the tenter. The water content (volatile content ratio) of PVA film was 31% before the initiation of stretching and 1.5% after the drying.

- The difference in the conveyance speed between right  
25   and left tenter clips was less than 0.05% and the angle

made by the center line of film introduced and the center line of film delivered to the next step was  $0^\circ$ . Here,  $|L1-L2|$  was 0.7 m, W was 0.7 m and a relationship of  $|L1-L2|=W$  was established. At the outlet of the tenter, wrinkling and deformation of film were not observed.

Then, the PVA film was attached with saponified Fujitac (cellulose triacetate, retardation value: 3.0 nm) produced by Fuji Photo Film Co., Ltd., using an aqueous 3% PVA (PVA-117H produced by Kuraray Co., Ltd.) solution as the adhesive and further dried at  $80^\circ\text{C}$  to obtain a polarizing plate having an effective width of 650 mm.

The absorption axis direction of the obtained polarizing plate was inclined at  $45^\circ$  with respect to the longitudinal direction and also inclined at  $45^\circ$  with respect to the phase lag axis of Fujitac.

The transmittance of this polarizing plate at 550 nm was 43.3% and the polarization degree was 99.98%.

The polarizing plate obtained was subjected to tests of heat resistance and humidity and heat resistance, as a result, the fluctuation width of the single plate transmittance was 13.5% and the fluctuation width of the polarization degree was 12.7%.

As apparent from the comparison of Comparative Example 5 with Examples 13 and 15, by using PVA having a high polymerization degree or a metal salt, the fluctuation



width in the transmittance and polarization degree after the test of heat resistance and humidity and heat resistance can be reduced without causing decoloration or discoloration.

5        Also, from the comparison between Examples 13 and 14, it is apparent that by using zinc out of metal salts, the fluctuation width in the transmittance and polarization degree after the test of heat resistance and humidity and heat resistance can be more reduced. Furthermore, from the  
10 comparison between Examples 14 and 16, it is seen that by using PVA having a high polymerization degree and a metal salt in combination, the fluctuation width in the transmittance and polarization degree after the test of heat resistance and humidity and heat resistance can be  
15 minimized.

#### Industrial Applicability

The present invention can provide a polarizing plate having excellent dimensional stability, particularly aging  
20 stability, a method for easily producing a polarizing plate, being capable of improving the yield in the step of punching the polarizing plate, and a liquid crystal display having excellent display grade at a low cost.

## CLAIMS

1. A polarizing plate comprising:  
a polarizing film; and  
a protective film attached to at least one surface of  
5 the polarizing film,  
wherein the angle made by the stretching axis of the  
protective film and the stretching axis of the polarizing  
film is no less than  $10^\circ$  and less than  $90^\circ$ .
- 10 2. The polarizing plate as claimed in claim 1,  
which is a long polarizing plate in a roll-form, wherein  
the protective film having a stretching axis in parallel to  
the longitudinal direction is attached to at least one  
surface of the polarizing film having a stretching axis  
15 neither in parallel nor perpendicular to the longitudinal  
direction.
3. A long polarizing film having:  
an absorption axis neither in parallel nor  
20 perpendicular to the longitudinal direction;  
a polarization degree of 90% or more at 550 nm;  
a single plate transmittance of 35% or more at 550  
nm; and  
a dispersion of an angle of the stretching axis to  
25 the longitudinal direction of within  $\pm 0.5^\circ$ , when the angle

is measured in the cross direction.

4. A long polarizing film having:  
an absorption axis neither in parallel nor  
5 perpendicular to the longitudinal direction;  
a polarization degree of 90% or more at 550 nm;  
a single plate transmittance of 35% or more at 550  
nm;  
a dispersion of the in-plane polarization degree of  
10 within  $\pm 0.5\%$ ; and  
a dispersion of the single plate transmittance of  
within  $\pm 0.5\%$ .

5. A long polarizing film having:  
15 an absorption axis neither in parallel nor  
perpendicular to the longitudinal direction;  
a polarization degree of 80% or more at 550 nm;  
a single plate transmittance of 35% or more at 550  
nm; and  
20 a surface roughness: Ra of 10  $\mu\text{m}$  or less.

6. The polarizing plate as claimed in claim 2,  
wherein

- (a) the polarizing film has an absorption axis  
25 neither in parallel nor perpendicular to the longitudinal

direction,

the polarizing plate has a single plate transmittance of 40% or more at 550 nm and a polarization degree of 95% or more at 550 nm, when the polarization degree is  
5 calculated by formula (1) below, and

(b) when the polarizing plate is left standing in an atmosphere at a temperature of 60°C and a humidity of 90% for 500 hours, the polarizing plate has:

(b-1) a fluctuation width of the transmittance at 550  
10 nm of within  $\pm 10\%$ , as compared with the initial value; and

(b-2) a fluctuation width of the polarization degree at 550 nm of within  $\pm 10\%$ , as compared with the initial value:

Formula (1)

15 
$$P = [(H0 - H1) / (H0 + H1)]^{1/2} \times 100$$

wherein H0 is a transmittance (%) when two polarizing plates are superposed so that the absorption axes are agreed, and H1 is a transmittance (%) when two polarizing plates are superposed so that the absorption axes are  
20 orthogonalized.

7. The long polarizing film as claimed in claim 5, wherein the number of color slippage streaks is 4 or less per 1 m<sup>2</sup>.

8. The polarizing plate as claimed in claim 1, 2 or 6, wherein the protective film is a transparent film and the retardation of the polarizing plate at 632.8 nm is 10 nm or less.

5

9. A method for producing a polarizing plate, comprising attaching a stretched protective film in a roll-form to at least one surface of a polarizing film,

wherein the polarizing film is produced by a method  
10 for stretching a polymer film, comprising:

holding both edges of a continuously fed polymer film by holding means; and

stretching the film, while travelling said holding means to the longitudinal direction of the film and applying tension to the film,  
15

wherein, when L1 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at one edge of the polymer film, L2 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at the other edge of the polymer film, and W represent a distance between the two substantial holding release points, L1, L2 and W satisfy a relation represented  
20 by formula (2) below, and the difference in the  
25

conveyance speed in the longitudinal direction between right and left film gripping means is less than 1%:

Formula (2)

5  $|L2-L1| > 0.4W$

10. The method for producing a polarizing plate as claimed in claim 9, wherein the polymer film is stretched while keeping the supporting property of the polymer film  
10 and allowing a volatile content ratio of 5% or more to be present, and then is shrunk while reducing the volatile content ratio.

11. The method for producing a polarizing plate as  
15 claimed in claim 9, wherein the polymer film for the polarizing film is a polyvinyl alcohol-base film.

12. The method for producing a polarizing plate as claimed in claim 10, wherein, when the polymer film is  
20 shrunk while reducing the volatile content ratio, a reduction rate of the volatile content ratio is 1%/min.

13. The method for producing a polarizing plate as claimed in any one of claims 9 to 12, wherein an angle made  
25 by the longitudinal direction and the absorption axis

direction of the polarizing film is from 20 to 70°.

14. The method for producing a polarizing plate as claimed in claim 13, wherein the angle made by the longitudinal direction and the absorption axis direction of the polarizing film is from 40 to 50°.

15. The method for producing a polarizing plate as claimed in any one of claims 9 to 14, which comprises:

10 drying the stretched polymer film for the polarizing film to shrink and reduce the volatile content ratio;  
attaching the protective film to at least one surface of the polymer film after or during the drying; and  
heat-treating the laminate of the protective film and  
15 the polymer film.

16. A method for producing a polarizing plate, comprising attaching a stretched protective film in a roll-form to at least one surface of a polarizing film, the  
20 polarizing film having:

a polarization degree of 80% or more at 550 nm;  
a single plate transmittance of 35% or more at 550 nm; and

a surface roughness: Ra of 10  $\mu\text{m}$  or less,  
25 wherein the polarizing film is produced by a method

for stretching a polymer film, comprising:

holding both edges of a continuously fed polymer film by holding means; and

5 stretching the film while travelling said holding means to the longitudinal direction of the film, and while applying tension to the film;

10 wherein, when L1 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at one edge of the polymer film, L2 represents a trajectory of the holding means from a substantial holding start point until a substantial holding release point at the other edge of the polymer film, and W represent a distance between the two substantial holding release points, L1, L2 and W satisfy a relation represented by formula (2):  $|L2-L1| > 0.4W$ ,

15 the polymer film for the polarizing film has an elastic modulus of from 0.1 to 500 MPa before stretching, and

20 the polymer film is stretched while keeping the supporting property of the polymer film, and while allowing a volatile content ratio of 5% or more to be present, and then is shrunk while reducing the volatile content ratio.

25



17. The method for producing a polarizing plate as claimed in claim 16, wherein the polymer film for the polarizing film is a film of a polyvinyl alcohol having a number average polymerization degree of 2,000 to 5,000.

5

18. The method for producing a polarizing plate as claimed in claim 16, wherein the method for stretching the polymer film for the polarizing film comprises a step of adding a metal salt.

10

19. The method for producing a polarizing plate as claimed in claim 18, wherein the step of adding a metal salt is a step of dipping the polymer film in a solution containing a metal salt.

15

20. The method for producing a polarizing plate as claimed in claim 19, wherein a metal salt concentration in the solution containing a metal salt is from 0.01 to 10.0 wt%.

20

21. The method for producing a polarizing plate as claimed in any one of claims 9 to 15, wherein the distribution of the volatile component content in the film for the polarizing film is 5% or less before stretching.

25

22. The method for producing a polarizing plate as claimed in claim 16, wherein, after attaching a stretched protective film in a roll-form to at least one surface of the polarizing film, the laminate of the polarizing film and the protective film is subjected to an after-heating.

23. A liquid crystal display comprising a liquid crystal cell and polarizing plates disposed in both sides of the liquid crystal cell,

10 wherein at least one of the polarizing plates is a polarizing plate punched out from at least one selecting from the group consisting of:

the polarizing plate described in claims 1, 2 or 6;

15 a polarizing plate having at least one of the polarizing films described in claims 3, 4, 5 and 7; and

a polarizing plate produced by the method described in any one of claims 9 to 22.

FIG. 1

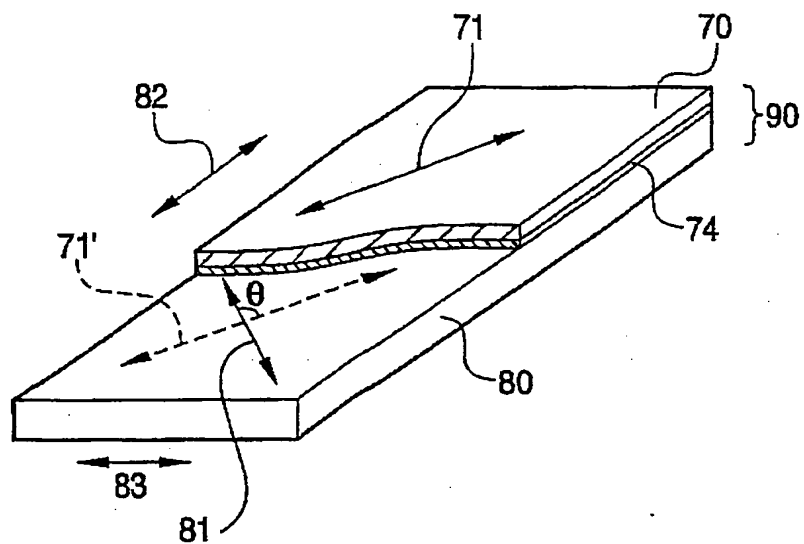
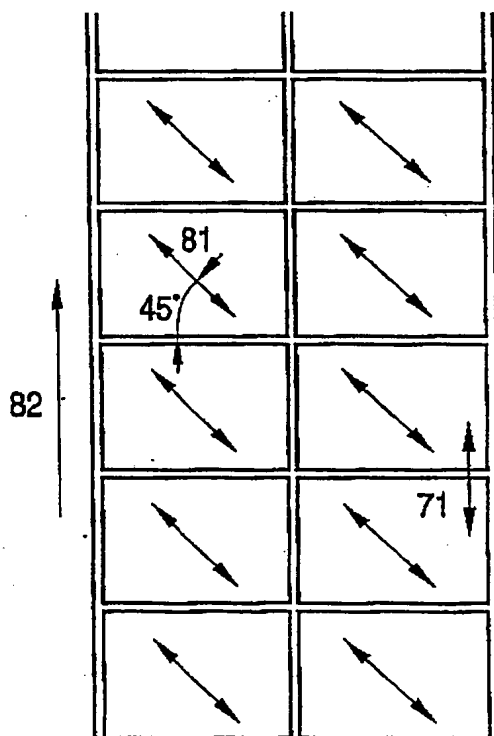
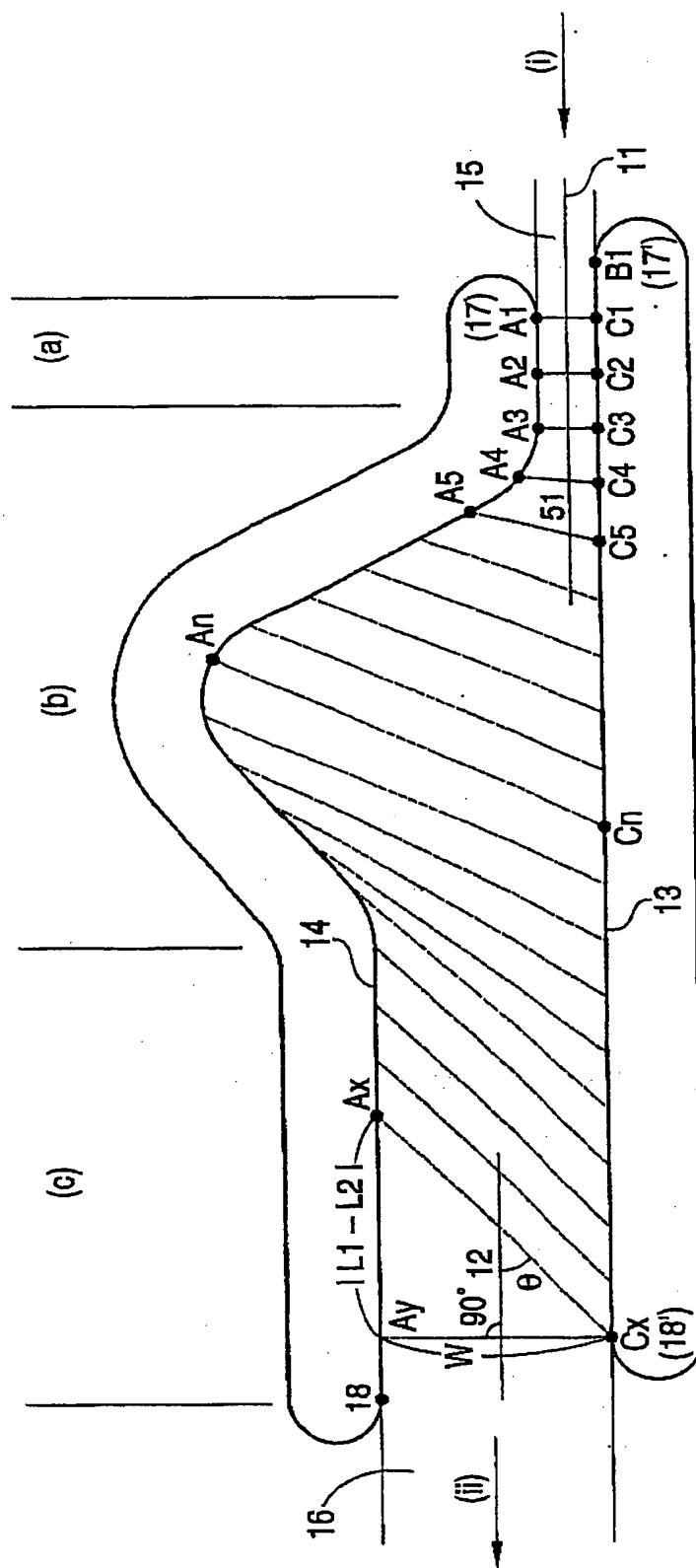


FIG. 2



**FIG. 3**



**FIG. 4**

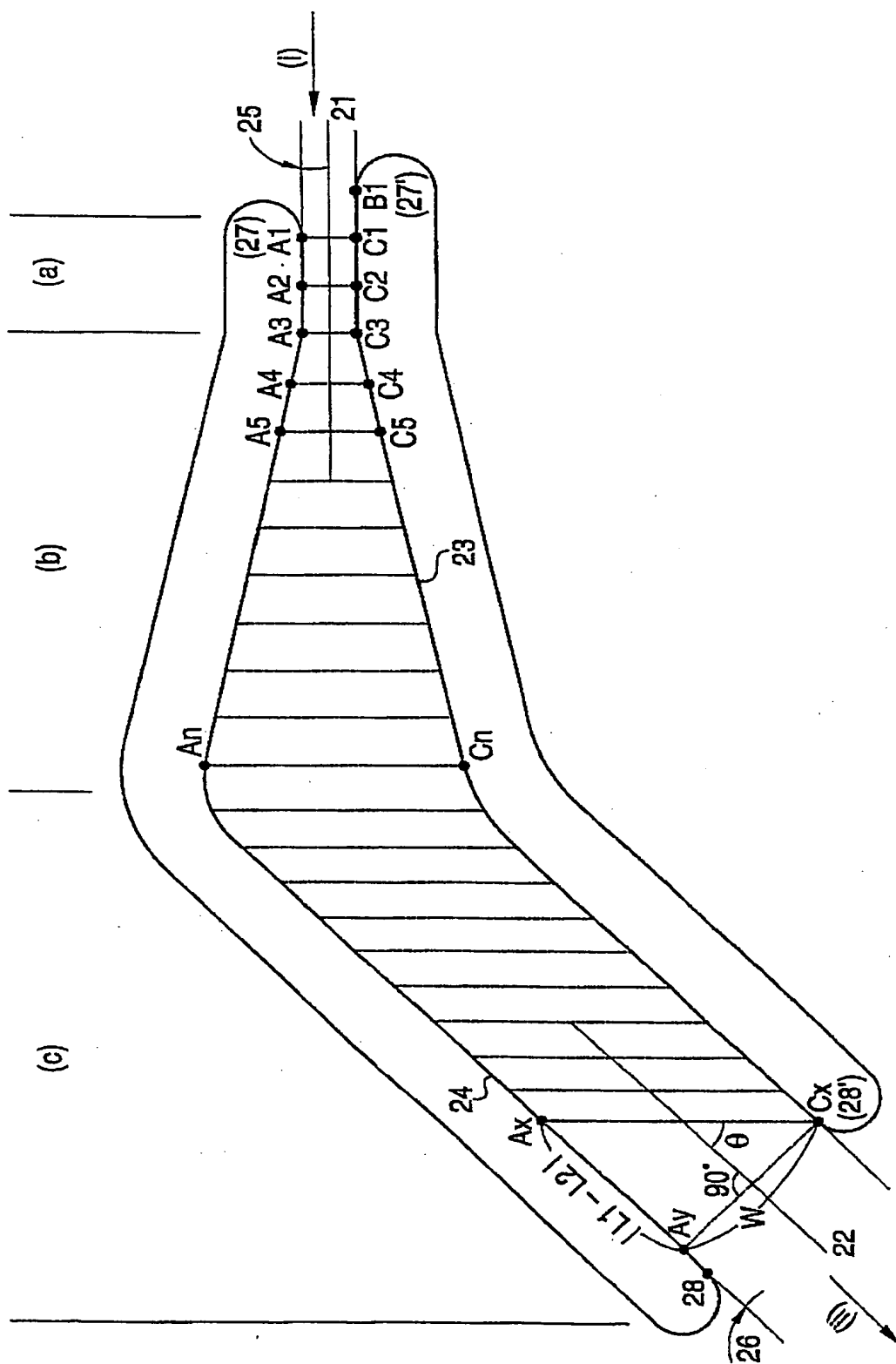


FIG. 5

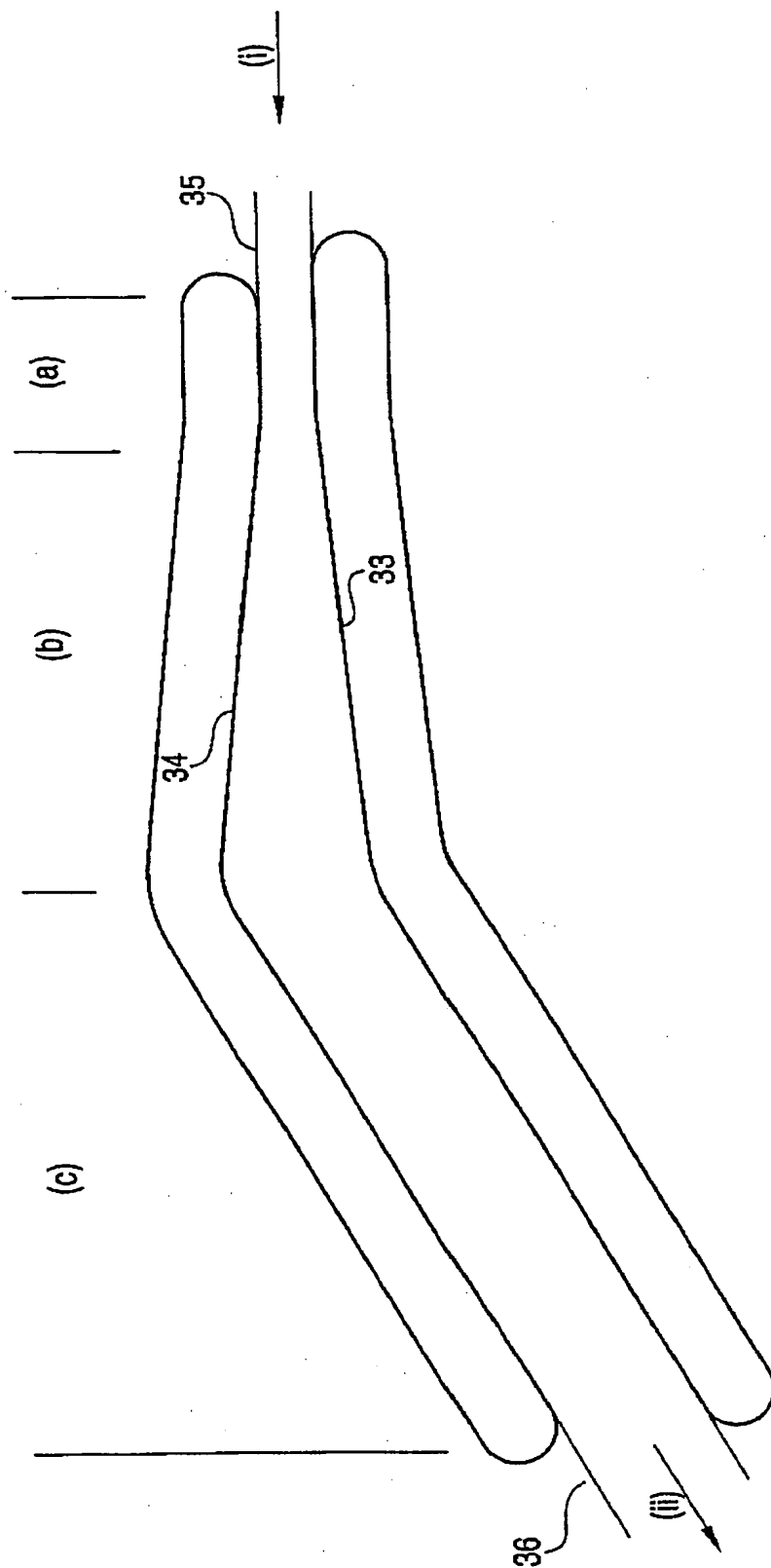


FIG. 6

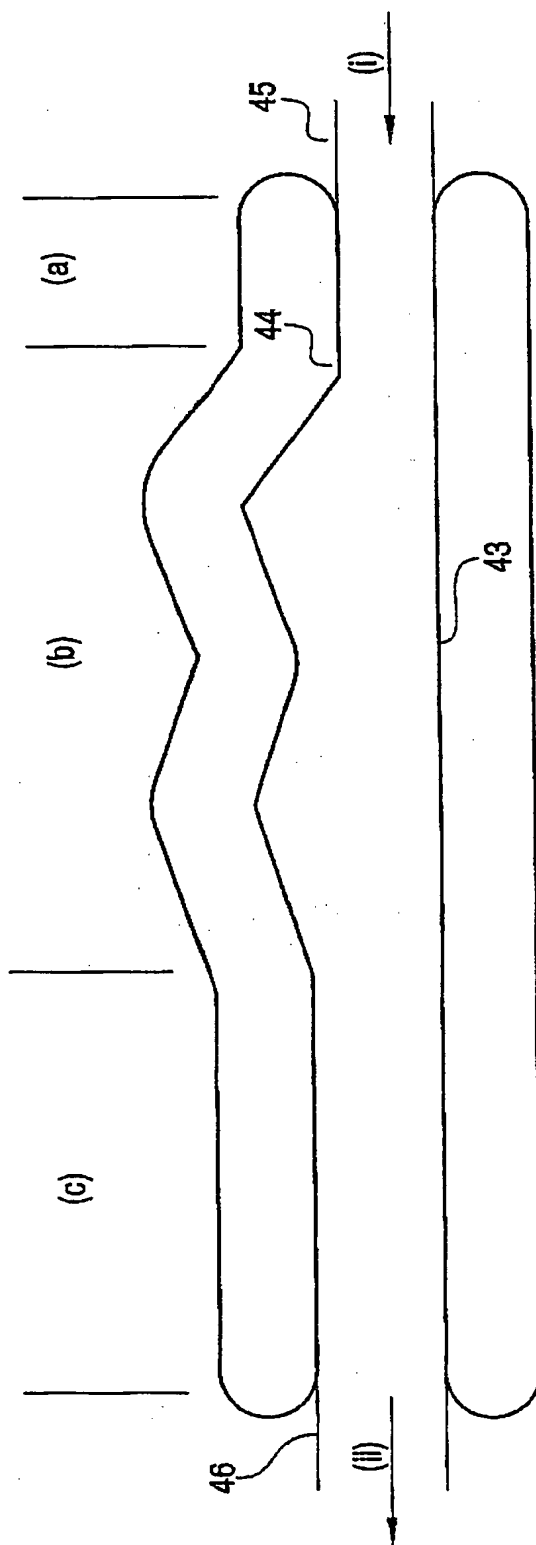
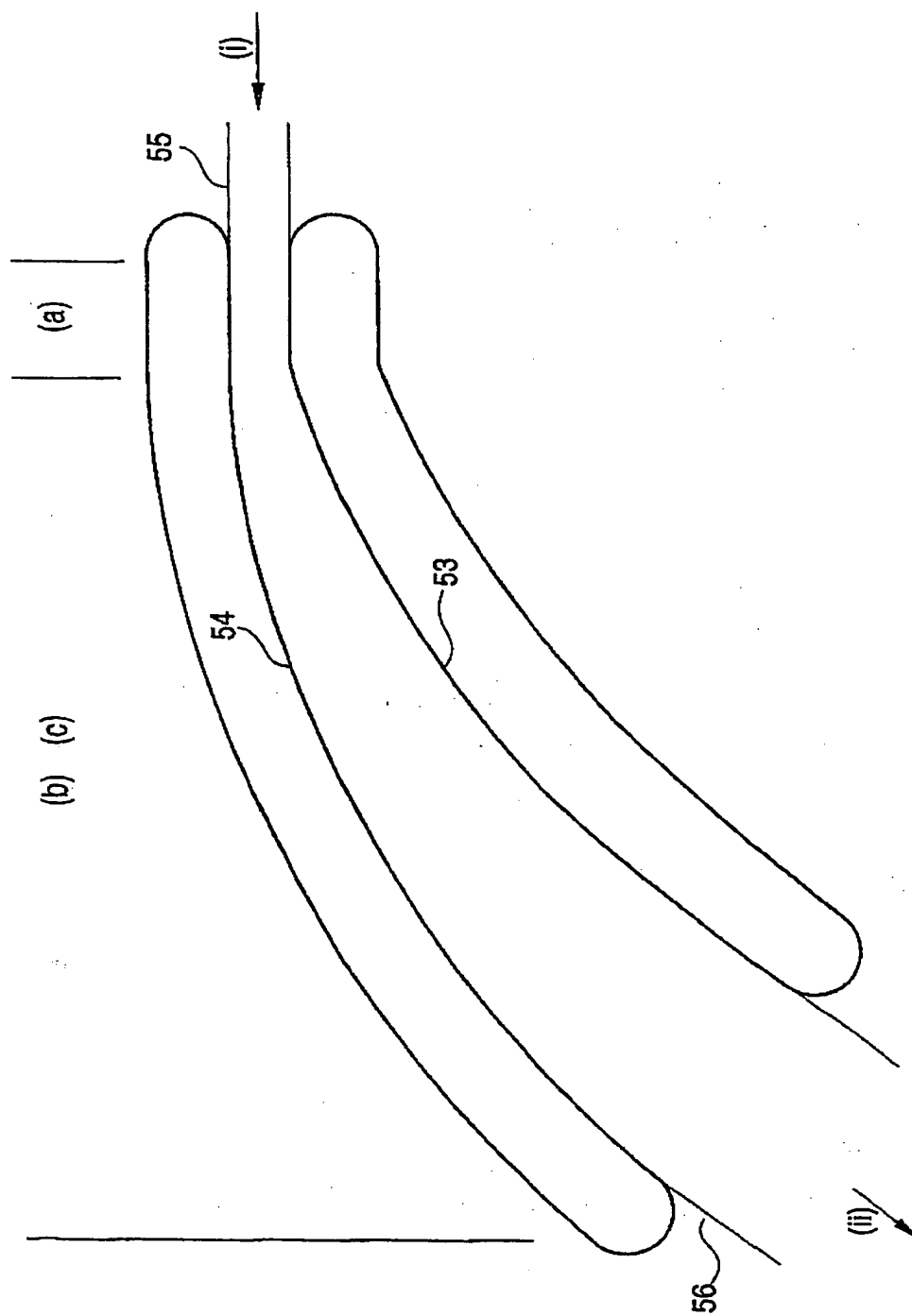
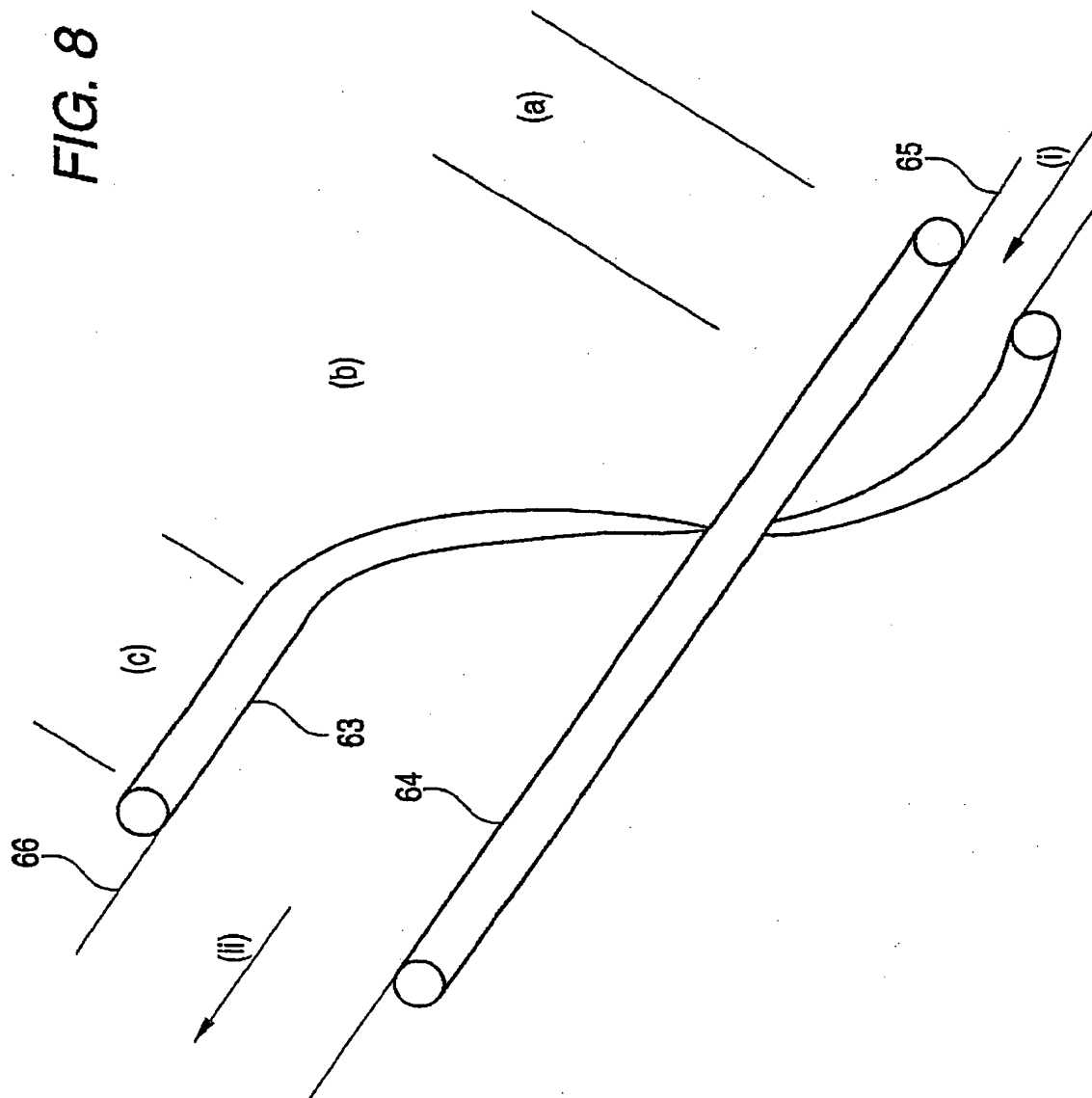


FIG. 7







*FIG. 9*

91
97
92
98

FIG. 10

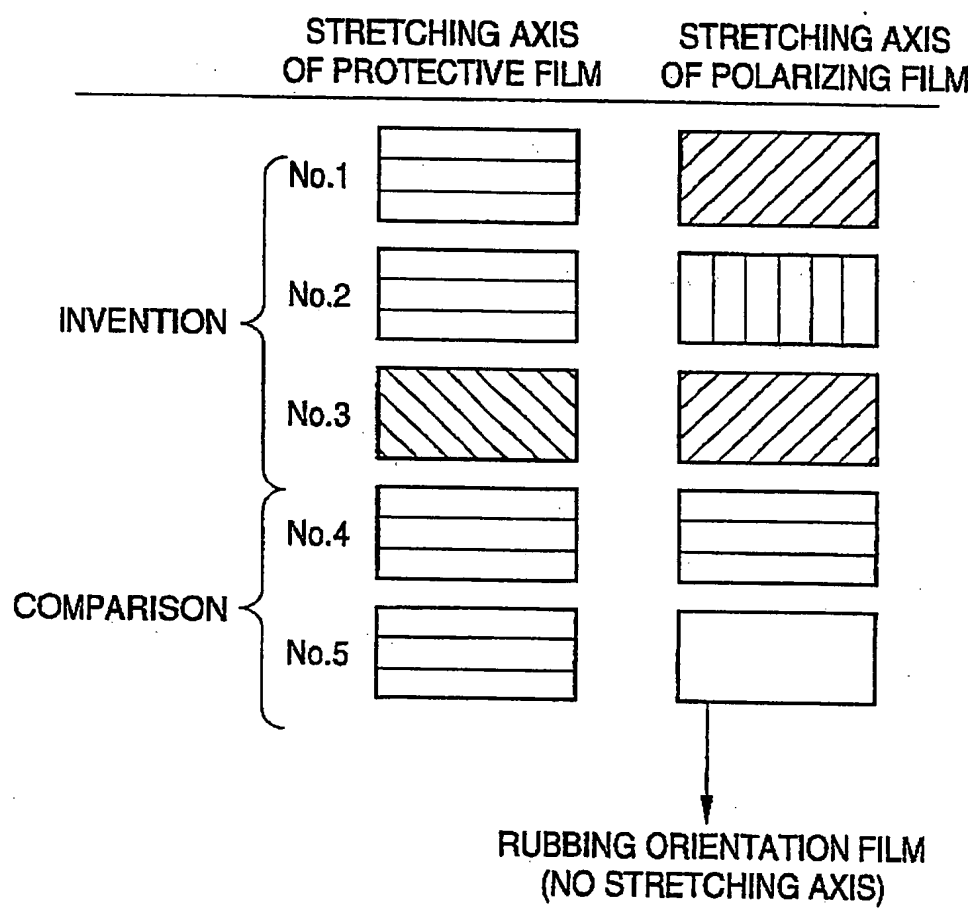


FIG. 11

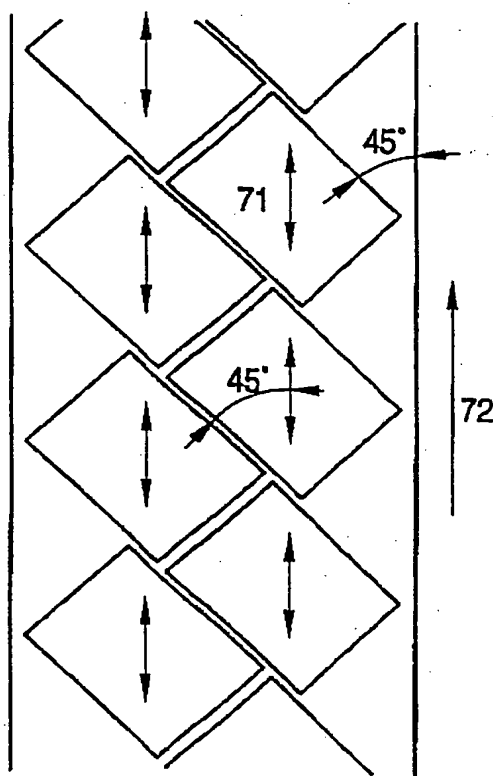


FIG. 12

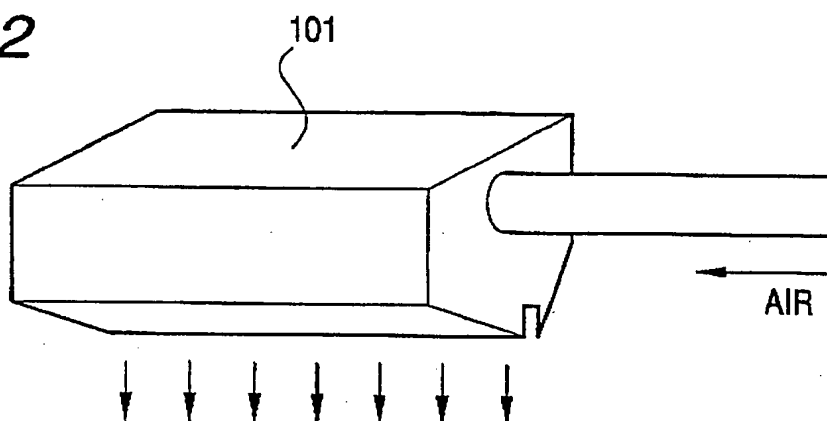


FIG. 13

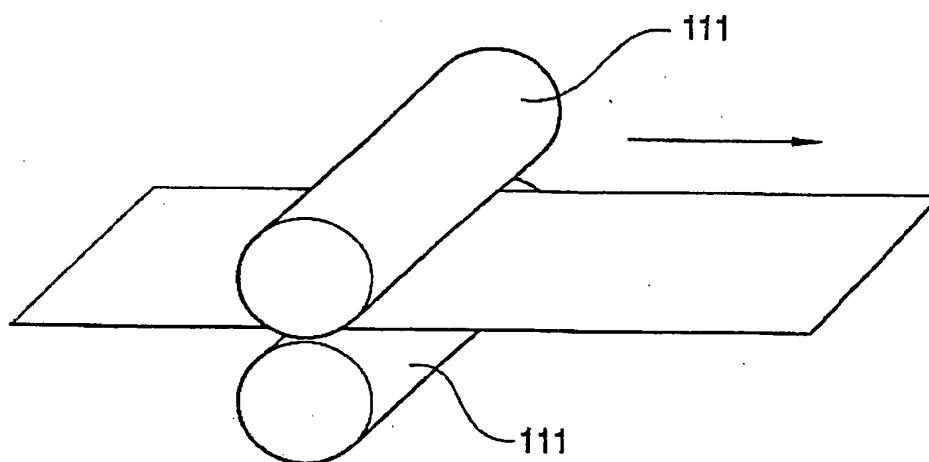


FIG. 14

